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## BULLETIN OF THE ACADEMY OF SCIENCES OF THE USSR

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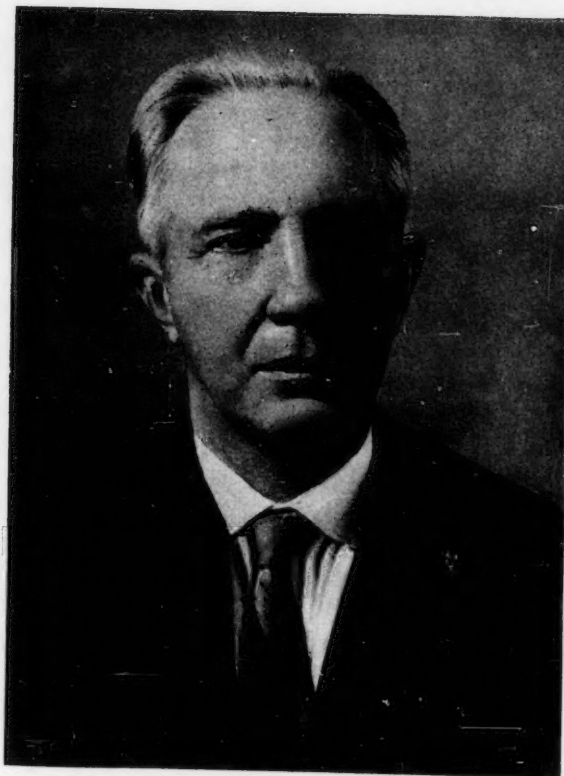
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SECRET



MIKHAIL MIKHAILOVICH DUBININ

Translated from Izvestiya Akademii Nauk, Otdelenie Khimicheskikh Nauk, No. 1, p. 3,  
January, 1961

Dear Mikhail Mikhailovich,

The Presidium of the Academy of Sciences, Division of Chemical Science and the Editorial Board of the journal "Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk" cordially congratulate you on your sixtieth birthday.

Being an outstanding specialist in the field of sorption processes, adsorbent structures, sorption techniques, and gas defense techniques, you have initiated a number of original lines of research which are being developed successfully in your school and are of fundamental importance in science. One of these lines was the classical potential theory of adsorption you developed and the system of concepts and mathematical technique based on it, which have converted this theory into a vigorous method for solving scientific and practical problems.

For a number of years you have directed successfully the Division of Chemical Science of the Academy of Sciences USSR and are a member of the Presidium of the Acad. Sci. USSR.

You are known in the scientific world not only as a scientist who has strived to maintain the scientific link with foreign schools in the interests of Soviet science, but also as an active participant in the Pugwash Conference for the Defense of Peace on Earth.

The Soviet Government has valued your services highly. You have been awarded the Order of Lenin, two Orders of the Red Star, the Order of the National War, and the Stalin Prize twice.

We wish you, dear Mikhail Mikhailovich, health and further success in your indefatigable activity and continued sound reasoning.

The Presidium of the Academy of Sciences, USSR,  
Division of Chemical Sciences, Academy of  
Sciences, USSR  
Editorial Board of "Izvestiya Akademii Nauk,  
Otdelenie Khimicheskikh Nauk"

# INORGANIC AND ANALYTICAL CHEMISTRY

## APPLICATION OF THE EMANATION METHOD TO THE STUDY OF CONVERSIONS OF HETEROPOLY COMPOUNDS

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and A. M. Babeshkin

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Translated from *Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk*,

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Emanation methods are now assuming great importance in the investigation of structural conversions in solids [1-5]. In the present work, the emanation method was used for studying phenomena occurring during the dehydration and thermal decomposition of heteropoly compounds. As the subject of the investigation we chose the barium salt of phosphotungstic acid and this was labeled with the radium isotope thorium X, which continuously liberates thorium emanation. Due to the isomorphism of radium and barium compounds, a uniform distribution of radium atoms was to be expected on coprecipitation with the barium salt.

Tribarium phosphotungstate  $3\text{BaO} \cdot \text{P}_2\text{O}_5 \cdot 24\text{WO}_3 \cdot x\text{H}_2\text{O}$  has been studied comparatively little; its hydrates in which the number of water molecules  $x = 63, 58, 48$ , and  $46$  have been described [6-11]. The 48-water hydrate, which forms octahedral crystals [8], was investigated by the powder x-ray diffraction method [10]. The literature contains no information on the conditions of dehydration and thermal decomposition of this salt.

### EXPERIMENTAL

Phosphotungstic acid was prepared by the ether method [12, 13] from sodium tungstate and disodium phosphate in hydrochloric acid. The barium salt was prepared by titration of the solution of the acid with the calculated amount of 0.1 M  $\text{BaCl}_2$ . The acidity of the final solution was pH 0.1-1.5. The precipitate consisted of colorless, lustrous crystals of octahedral form. The barium phosphotungstate was moderately soluble in water at normal temperature and readily soluble on heating. It effloresced in air and turned to a fine white powder. Depending on the drying conditions (in air or over sulfuric acid), the water content of the salt varied from 16 to 48 molecules.

The phosphotungstic acid and its barium salt were analyzed for water, phosphorus, tungsten, and barium [13, 14]. The water was determined by firing a sample of the substance to constant weight at  $600^\circ$ , the phosphorus in the form of magnesium pyrophosphate, and the tungsten by precipitation with quinoline acetate after removal of the phosphorus. Separate samples were used for the determination of barium. The whole of the heteropolyanion was precipitated with quinoline acetate and after the complete removal of organic substances barium sulfate was precipitated from the filtrate. Below we give the results of an investigation of the preparation which had been dried for 12 hr in a desiccator over 96% sulfuric acid. The analysis corresponds to the formula  $2.98\text{BaO} \cdot \text{P}_2\text{O}_5 \cdot 24\text{WO}_3 \cdot 19\text{H}_2\text{O}$ , which is close to that of the tribarium salt.

TABLE 1

|               | $\text{WO}_3$ | $\text{P}_2\text{O}_5$ | $\text{H}_2\text{O}$ | $\text{BaO}$ |
|---------------|---------------|------------------------|----------------------|--------------|
| Found, %      | 85.34         | 2.17                   | 5.18                 | 6.94         |
| Calculated, % | 85.74         | 2.18                   | 5.15                 | 6.98         |

Simultaneously with the inactive salt, we prepared a salt containing radium-224 (thorium X).

The radium-224 was separated from the mother isotope thorium-228 (radiothorium) by the ion-exchange method we developed. A hydrochloric acid (2 N) solution of thorium-228 in equilibrium with radium-224 was passed through a column packed with KU-2 resin in the acid form. The thorium ions were adsorbed in the upper part of the column, while the radium ions passed into the filtrate completely. After being washed with water, the column could be used for a repeat extraction of radium-224 after a time interval suitable for its accumulation. The filtrate containing the radium-224 was evaporated to dryness. The radium-224 was washed out with a definite amount (10-15 ml) of 0.1 N barium chloride solution and then used for the preparation of active barium phosphotungstate. The active and inactive salts were prepared and dried under identical conditions and we simultaneously took samples of the inactive salt for analysis, and of the active salt for studying the emanation.

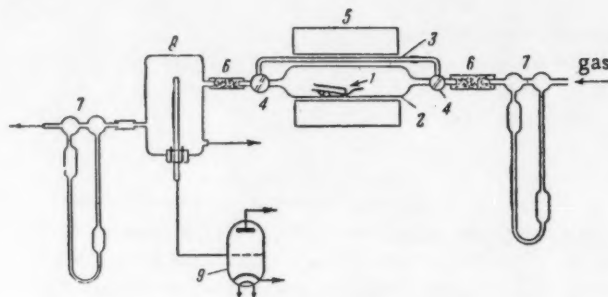


Fig. 1. Plan of apparatus: 1) Quartz boat with tube; 2) quartz tube; 3) tube for passing air when the background of the chamber was measured; 4) taps; 5) furnace; 6) drying agents; 7) rheometers; 8) ionization chamber; 9) schematic representation of pulse amplifier.

The emanation was studied on the apparatus whose plan is shown in Fig. 1. A sample of the active salt in a small quartz test tube was placed in a quartz tube, which lay in a furnace. Another tube was attached in parallel with the furnace for measuring the background of the chamber during an experiment. Air dried with anhydron together with the thoron entered the ionization chamber, which was connected to an apparatus of the Da type [15]. The size of the sample of the salt investigated was chosen so that the recorded activity gave measurements of sufficient accuracy. Preliminary experiments showed that heating curves of salt samples of the same composition were identical and readily reproducible under the conditions chosen (Fig. 2).

Figure 3 gives generalized heating curves of barium phosphotungstate preparations with various initial water contents ( $x \cdot \text{H}_2\text{O}$ ), depending on the conditions under which the salt was prepared. For the experiments we used the following preparations: No. 1 (curve 1) - air-dried salt;  $x = 48$ ; No. 2 (curve 2) - salt dried for 17 hr in a desiccator over concentrated sulfuric acid;  $x = 19$ ; No. 3 (curve 3) - salt dried in a stream of air, preliminarily dried with anhydron;  $x = 17$ ; No. 4 (curve 4) - salt dried for 43 hr over concentrated sulfuric acid;  $x = 15-16$ .

The initial sections of the emanation curves differed in accordance with the different water contents of the preparations (Fig. 3). The salt which had been dried in air at room temperature showed the highest emanating power and the emanation factor reached almost 75%, while partly dehydrated preparations showed a lower emanating power. The emanation was least with the preparation which had been kept over concentrated sulfuric acid for 43 hr. It should be noted that a decrease in emanating power for hydrates with a lower water content has been observed by many investigators [2, 16]. While the air-dried salt showed a rapid fall in emanating power with a rise in temperature, the other preparations showed a rise in emanating power up to 40° with characteristic peaks at 40-45°. There was a check in the fall in emanation at this temperature on the curve of the air-dried salt. The emanation curves of both the air-dried salt and partly dehydrated preparations were the same above 60°, regardless of the initial amount of bound water. Consequently, the composition and behavior of the preparations became identical at this temperature.

The emanating power fell rapidly with a rise in temperature to 65-70°; it was then a factor of approximately 12 less than the original value for the air-dried salt. Over the temperature range of 70-75°, all the preparations showed an appreciable increase in emanating power from 6 to 11% with a new fall at temperatures of 85-95°. A further rise in temperature produced a fall in emanation with a minimum at 260°. The general, though slight,

decrease in emanation over the range of 85-260° may also be associated with the removal of water. The slight increase in emanation over the range of 260-475° was caused by diffusion liberation of the emanation and was not connected with a structural change [5]. At 450-490° there was a sharp rise in emanation. The slight decrease in emanation at ~520 is reminiscent of sections on the emanation curves of powdered solids in the sintering region. A sharply expressed emanation peak at 580° was followed by a rapid fall in emanation up to 605°.

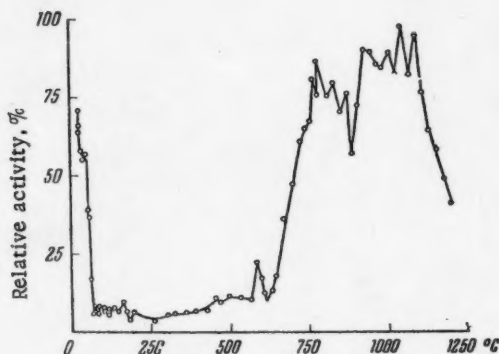


Fig. 2. Generalized emanation polytherm.

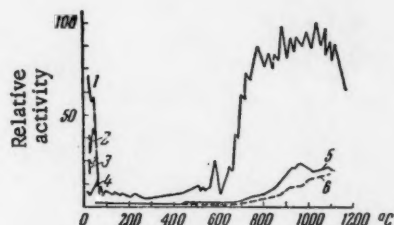


Fig. 3. Emanation polytherms: Curves 1-4) hydrates with various water contents; 5) reheating of sample No. 1; 6) cooling curve of sample No. 1.

The emanation maximum (580°) and minimum (605°) were absent from curves for reheating of the preparation (Fig. 3). These effects were apparently caused by decomposition of the heteropolyanion, which was also confirmed by a change in the color of the preparation, but could hardly be detected by the thermogravimetric method. Over the range of 675-710° there was a rapid, discontinuous increase in emanation from 20 to 60%. A similar rapid increase in emanation, which is connected with rearrangement of the crystal lattice, has been observed previously [5] for other compounds in the region of polymorphous conversions. In the high emanation region (~90%) above 700° it was possible to distinguish emanation peaks at 770-800°, 890-900°, 950-970°, and 1000-1050°. Maximum emanation corresponded to 1050°.

The complex picture of emanation in the high temperature region may be caused by polymorphous conversions, the formation of eutectic mixtures and solid solutions, and also reactions of the conversion products with the material of the container (quartz).

For comparison, we also studied the conversions of barium phosphotungstate by other methods, namely, thermogravimetric, thermographic, and x-ray structural methods.

The dehydration of the barium salt was studied on continuously-weighing balances with automatic recording. At the same time, the losses in weight were determined visually. The dehydration of barium phosphotungstate containing 19 water molecules is illustrated in Fig. 4 (curve 1). The heating rate was approximately 2° per min. Over the temperature range from 20 to 50°, 2 water molecules were lost, from 60 to 80° there was no loss of water, and at temperatures of 125-200°, there was the greatest loss of water. The horizontal section of the dehydration curve corresponds to the hydrate containing approximately 16 water molecules. An analogous dehydration curve was obtained for the 42 water hydrate (Fig. 4, curve 2), for which the heating rate was approximately 3 times greater. In this case 27 water molecules had been removed up to the horizontal section of the curve (95°). Subsequently, curve 2 practically coincided with curve 1. The last portions of water were removed over the range 200-400°. Thermogravimetric analysis indicated the existence of several hydrates of barium phosphotungstate containing 48, 42, 19, 16, and 1.5-1.0 water molecules and also phases of variable composition.

We also compared the solubilities of barium phosphotungstate and products of its heating. The 48-water hydrate dissolved completely in a 10-fold excess of water at room temperature. The solubility of the products from heating it to 200-400° differed little from the solubility of the starting salt. Since the salt that had been dehydrated at 400° still dissolved almost completely, it must be assumed that the heteropolyanion exists as such under the second conditions. With a rise in temperature to 600-800°, the soluble part of the fired product decreased sharply; then the colloidally soluble part of the preparations increased at 1100° (Table 2).

The thermographic analysis of barium phosphotungstate was carried out on a Kumakov pyrometer with differential recording. The thermograms were plotted over a period of one and half hours. Figure 5 gives one of the thermograms for a salt containing 19 water molecules.

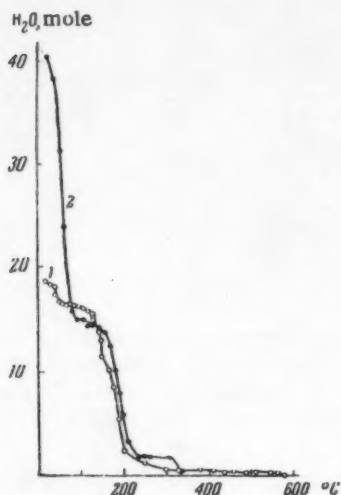


Fig. 4. Dehydration curves: 1) 19-water hydrate; 2) 48-water hydrate.

TABLE 2. Comparative Water-Solubility of Barium Phosphotungstate and Its Heating Products

| Heating temperature, °C | Amount of water in salt, mole | Soluble portion, % |
|-------------------------|-------------------------------|--------------------|
| 17-19                   | 48                            | 100                |
| 200                     | 2                             | 94                 |
| 400                     | 0                             | 84,6               |
| 600                     | —                             | 0,23               |
| 800                     | —                             | 0,06*              |
| 1100                    | —                             | 0,45**             |

\* A colloiddally soluble part appeared.

\*\* The colloiddally soluble part was clearly expressed.

salt heated to 460°, salt heated to 600° (insoluble part), salt heated to 800° (colloiddally soluble part), and salt heated to 1100° (colloiddally soluble part).

Comparison of the interplanar distances and reflection intensities for the 40-water hydrate of barium phosphotungstate with data obtained previously [10] for the 48 water hydrate indicated that these substances have different crystal structures. The crystal structure of the salt obtained by firing to 460° ( $x \approx 0,5$ ) differed from the structures of the higher hydrates. Hence it follows that the nature of the crystal structure is connected with the amount of water present. All the salts given above, i.e., the 48-water and 40-water hydrates and the practically anhydrous salt, had a structure with a large elementary cell.

The insoluble part of the salt heated to 600° had a primitive cubic elementary lattice of relatively heavy tungsten atoms, the size of which was substantially less than that of the starting salt. The appearance of this structure may be associated with the destruction of the heteropolyanion. An analogous result was obtained for

\* The x-ray diffraction investigations were carried out by A. A. Babad-Zakhryapin in the Institute of Physical Chemistry, Academy of Sciences USSR.

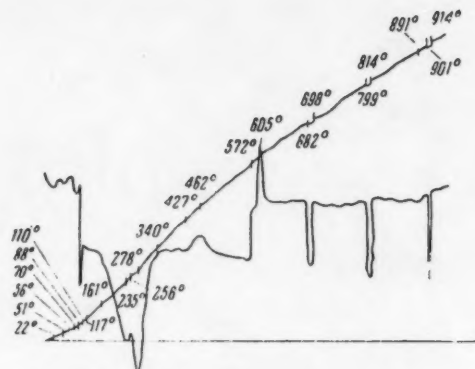


Fig. 5. Thermogram of 19-water hydrate of barium phosphotungstate.

Endothermal effects were recorded at temperatures of 50°, 88-100-110°, 150-235°, 256-278°, 572° (weakly expressed) 682-694°, 799-814°, and 907-917°. Exothermal effects were observed at temperatures of 462 and 605°. It is noteworthy that there was almost complete agreement (apart from the last three endothermal effects) between thermograms of barium phosphotungstate and literature data for the acid [17]. This indicates the identical nature of the water lost by the acid and the salt at temperatures up to 300°. The thermograms, which were recorded at a relatively high heating rate and were less clear than the emanation polytherms, indicated the existence of several salt hydrates and decomposition of the heteropolyanion above 450°.

For x-ray diffraction investigations,\* the samples were prepared by heating the salt in a stream of air to a definite temperature, i.e., under the conditions of the emanation experiments. The following samples were investigated: The starting salt containing 40 water molecules,

phosphotungstic acid [18]. At 600° and above, lines characteristic of tungsten trioxide appeared with increasing clarity both for the firing products themselves and for the insoluble part. The colloiddally soluble part of the products fired up to 1100° showed lines characteristic of barium phosphate, which is a final decomposition product together with tungsten trioxide.

#### DISCUSSION OF EXPERIMENTAL RESULTS

The general form of the emanation polytherms of barium phosphotungstate hydrates reflects the changes in the salt occurring during heating. A definite emanation value corresponds to each hydrate and this is smaller the lower the water content. On the emanation curves of preparations of different degrees of hydration, the conversions of the hydrates were reflected by small maxima (preparations 2, 3, and 4) or a check in the decrease in emanation (preparation 1). Corresponding to these data, in the low-temperature region the thermogram shows several endothermal effects, which are evidently connected with stepwise dehydration of the salts. The dehydration curves also show the existence of a 16-water hydrate and phases of variable composition. The emanation minimum at 260° corresponded to an endothermal effect on the thermogram and this may also be connected with the slow removal of water. Thermogravimetric analysis showed the presence of 0.8-1.0 water molecules at this temperature. The last portions of water are removed at ~350°. On this section there was a small increase in emanation, caused by the removal of the residual bound water, which facilitated the liberation of emanation due to diffusion. Had there been decomposition of the heteropolyanion of the salt in this region, it would have been accompanied by a considerable change in emanation and this was not observed.

The rise in the emanation curve up to 460° observed corresponds, then, to loosening of the lattice of the heteropolyanion; this is followed by a small decrease in emanation over the temperature range of 460-520°, which is probably connected with sintering that normally accompanies loosening. This process was reflected on the thermogram by an exothermal effect at 462°. The emanation maximum at ~580° is connected with the beginning of decomposition of the heteropolyanion and the formation of disperse tungsten trioxide, whose presence was indicated by the x-ray diffraction investigations. A clearly expressed exothermal effect corresponds to the emanation minimum at 605°. At this temperature there may be crystallization of amorphous tungsten trioxide, which was observed previously in a study of phosphotungstic acid [17]. The subsequent nature of the emanation polytherms and the thermograms is connected with conversions of the decomposition products of the salt. A comparison of the emanation curves of the starting salt and the product from heating it once, and the cooling curve shows the presence of at least three polymorphous conversions of the heating products at ~710°, 785-790°, and 895° (Figs. 2 and 3). Polymorphous conversions of tungsten trioxide at 710 and 895° have been described in the literature [17].

Thus, the general form of the emanation curves and the results of thermographic and x-ray structural analysis of barium phosphotungstate show that when the hydrated salt is heated, the bulk of the water is lost up to 200°, complete dehydration is observed at ~350°, and the structure of the heteropolyanion is retained up to 460°, when the preparation contains hardly any bound water. Further heating leads to decomposition (580°) of barium phosphotungstate. Tungsten trioxide and barium phosphate were detected in the decomposition products. The emanation method has made it possible to extend the range of physicochemical investigations of heteropoly compounds. Emanation polytherms demonstrate over a wide range of temperatures the nature of changes occurring in a substance during heating: dehydration, loosening of the lattice and sintering, decomposition, and polymorphous conversions. The advantages of this method are its clarity, high sensitivity and quite good reproducibility.

#### SUMMARY

1. The emanation method was used to study the processes occurring during the heating of barium phosphotungstate.
2. The emanation of the salt at room temperature is higher, the higher its water content.
3. Regardless of the initial water content of the original hydrates, the changes occurring during heating above 60° are the same in character.
4. Over the temperature range from 100 to 200°, where a large amount of water is lost, dehydration is not accompanied by a substantial change in emanation.
5. Practically complete dehydration (350°) is not connected with the decomposition of the heteropolyanion, which is quite stable and begins to decompose at 580°.

6. Barium phosphate and tungsten trioxide were found among the thermal decomposition products of barium phosphotungstate.

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SYSTEMS WITH CONCENTRATED HYDROGEN PEROXIDE  
COMMUNICATION 22. 20 AND 0° ISOTHERMS OF THE TERNARY SYSTEM  
 $\text{Cd}(\text{OH})_2 - \text{H}_2\text{O}_2 - \text{H}_2\text{O}$

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As the elements zinc and cadmium occur in the same subgroup of the Periodic Table, one would expect them to form peroxide compounds of the same type. A previous paper [1] on peroxide compounds of zinc also contained

TABLE 1. Data on the 20° Isotherm of the Ternary System  $\text{Cd}(\text{OH})_2 - \text{H}_2\text{O}_2 - \text{H}_2\text{O}$

| Expt.<br>No. | Composition of<br>residue, wt. % |       | Composition of liquid<br>phase, wt. % |                        |                            | Solid phase   |
|--------------|----------------------------------|-------|---------------------------------------|------------------------|----------------------------|---|
|              | act. $\text{O}_2$                | CdO   | act. $\text{O}_2$                     | $\text{H}_2\text{O}_2$ | $\text{CdO} \cdot 10^{-3}$ |   |
| 30           | —                                | —     | —                                     | —                      | 1,78                       | $\text{Cd}(\text{OH})_2$  |
| 32           | 6,36                             | 56,22 | 3,55                                  | 7,55                   | 2,91                       | The same  |
| 42           | —                                | —     | 5,62                                  | 11,60                  | 5,66                       | $\text{Cd}(\text{OH})_2 + \text{CdO}_2 \cdot 2\text{H}_2\text{O}$                   |
| 36           | —                                | —     | 6,10                                  | 12,95                  | 3,58                       | $\text{CdO}_2 \cdot 2\text{H}_2\text{O}$  |
| 45           | —                                | —     | 6,32                                  | 15,83                  | 1,60                       | The same  |
| 47           | —                                | —     | 6,80                                  | 14,47                  | 2,88                       | » »   |
| 13           | 7,98                             | 44,25 | 7,92                                  | 16,83                  | —                          | » »   |
| 46           | —                                | —     | 8,47                                  | 17,96                  | 0,26                       | » »   |
| 9            | 9,44                             | 44,79 | 9,61                                  | 20,43                  | 2,80                       | » »   |
| 24           | 9,21                             | 44,81 | 10,97                                 | 23,32                  | 3,33                       | » »   |
| 18           | 10,17                            | 43,60 | 12,27                                 | 26,08                  | 3,41                       | $\text{CdO}_2 \cdot 2\text{H}_2\text{O} + \text{CdO}_2 \cdot 1,5\text{H}_2\text{O}$ |
| 43           | —                                | —     | 13,20                                 | 28,00                  | 3,11                       | $\text{CdO}_2 \cdot 1,5\text{H}_2\text{O}$  |
| 23           | 10,97                            | 42,83 | 13,52                                 | 28,74                  | 2,84                       | The same  |
| 28           | —                                | —     | 13,37                                 | 28,42                  | 3,00                       | » »   |
| 25           | 10,15                            | 44,58 | 13,84                                 | 29,42                  | —                          | » »   |
| 29           | —                                | —     | 13,98                                 | 29,72                  | 2,85                       | » »   |
| 11           | 12,06                            | 45,00 | 14,82                                 | 31,51                  | 2,83                       | » »   |
| 27           | —                                | —     | 15,56                                 | 33,00                  | 2,20                       | » »   |
| 48           | —                                | —     | 16,47                                 | 34,95                  | 1,07                       | » »   |
| 20           | 12,13                            | 44,50 | 18,12                                 | 38,50                  | 0,63                       | » »   |
| 3            | 13,97                            | 42,90 | 18,64                                 | 39,63                  | 1,03                       | » »   |
| 49           | —                                | —     | 21,38                                 | 45,45                  | 2,16                       | » »   |
| 15           | 14,45                            | 43,42 | 21,74                                 | 46,22                  | 2,42                       | » »   |
| 7            | 16,66                            | 41,27 | 23,18                                 | 49,28                  | —                          | » »   |
| 16           | 15,59                            | —     | 23,43                                 | 49,75                  | 2,61                       | » »   |
| 37           | —                                | —     | 24,23                                 | 51,51                  | 2,73                       | » »   |
| 34           | —                                | —     | 25,08                                 | 53,32                  | 3,34                       | $\text{CdO}_2 \cdot 1,5\text{H}_2\text{O} + \text{CdO}_2 \cdot \text{H}_2\text{O}$  |
| 35           | —                                | —     | 25,50                                 | 54,21                  | 3,24                       | $\text{CdO}_2 \cdot \text{H}_2\text{O}$   |
| 33           | —                                | —     | 25,83                                 | 55,03                  | 2,92                       | The same  |
| 19           | 17,80                            | 46,65 | 26,79                                 | 56,95                  | 2,18                       | » »   |
| 8            | 18,62                            | 43,41 | 27,98                                 | 59,48                  | 0,93                       | » »   |
| 4            | 18,67                            | 43,85 | 28,42                                 | 60,42                  | —                          | » »   |
| 12           | 20,22                            | 44,03 | 31,15                                 | 66,22                  | 0,96                       | » »   |
| 5            | 21,67                            | 44,09 | 34,21                                 | 72,73                  | 2,56                       | $\text{CdO}_2 \cdot \text{H}_2\text{O} + \text{CdO}_2 \cdot 0,5\text{H}_2\text{O}$  |
| 14           | 21,90                            | 45,63 | 35,18                                 | 74,74                  | 1,09                       | $\text{CdO}_2 \cdot 0,5\text{H}_2\text{O}$  |
| 6            | 23,28                            | 45,15 | 37,23                                 | 79,15                  | —                          | The same  |
| 17           | 22,98                            | 49,82 | 37,41                                 | 79,53                  | 0,69                       | » »   |
| 10           | 23,98                            | 42,75 | 40,48                                 | 86,06                  | 0,8                        | » »   |
| 26           | 24,82                            | 40,99 | 41,91                                 | 89,10                  | 1,58                       | » »   |

data on peroxide compounds of cadmium. In the literature, peroxide compounds of cadmium are regarded as: 1) pure peroxides with the composition  $\text{Cd}_2\text{O}_3$  [2, 3]; 2) chemical compounds of cadmium peroxide and hydroxide,  $\text{CdO}_2 \cdot \text{Cd}(\text{OH})_2$  [4, 5]; 3) cadmium peroxide hydrates  $\text{CdO}_2 \cdot 0.5\text{H}_2\text{O}$  [6, 7]; 4) hydrate-perhydrate compounds  $\text{CdO}_2 \cdot \text{H}_2\text{O} \cdot \text{H}_2\text{O}_2$  [8, 9].

The hydroperoxide structure  $\text{Cd}(\text{OOH}) \cdot (\text{OH})$  was proposed in later work [10-12]. This is not sufficiently definite. Considering the large number of zinc peroxides found by studying the solubility of the ternary system  $\text{Zn}(\text{OH})_2 - \text{H}_2\text{O}_2 - \text{H}_2\text{O}$  [1], it also seemed interesting to study the solid phases occurring in the ternary system  $\text{Cd}(\text{OH})_2 - \text{H}_2\text{O}_2 - \text{H}_2\text{O}$ .

## EXPERIMENTAL

The procedure used for investigating the system  $\text{Cd}(\text{OH})_2 - \text{H}_2\text{O}_2 - \text{H}_2\text{O}$  through the solubility was described previously [1]. "Chemically pure" grade cadmium hydroxide and distilled hydrogen peroxide without stabilizer were used. The residue and liquid phase were analyzed for active oxygen and cadmium oxide. The active oxygen was determined by titration with 0.1 N  $\text{KmnO}_4$  solution in the presence of  $\text{H}_2\text{SO}_4$ . The cadmium oxide in the residue was determined by precipitation as cadmium ammonium phosphate with subsequent firing to cadmium pyrophosphate. Due to its low solubility, the  $\text{CdO}$  in the liquid phase was determined colorimetrically [13] with dithizone on an FEK-2 electrophotocolorimeter.

Solubility isotherms of the ternary system  $\text{Cd}(\text{OH})_2 - \text{H}_2\text{O}_2 - \text{H}_2\text{O}$ . We first determined the time for the system to reach equilibrium, as indicated by a constant active oxygen content in the liquid phase and the residue. It was established that  $\sim 2$  hr was sufficient at  $0^\circ$  and  $\sim 1.5$  hr at  $20^\circ$ . In studying the ternary system  $\text{Cd}(\text{OH})_2 - \text{H}_2\text{O}_2 - \text{H}_2\text{O}$  at  $20$  and  $0^\circ$ , in order to decrease the possible errors in the determinations of the number and the limits of existence of the solid phases, we used additional diagrams of the  $\text{CdO}$  content in relation to the  $\text{H}_2\text{O}_2$  concentration in the liquid phase. In this case, the compositions of the solutions in equilibrium with two solid phases were checked graphically from the positions of the maxima on the solubility diagram of  $\text{CdO} - \text{H}_2\text{O}_2$ .

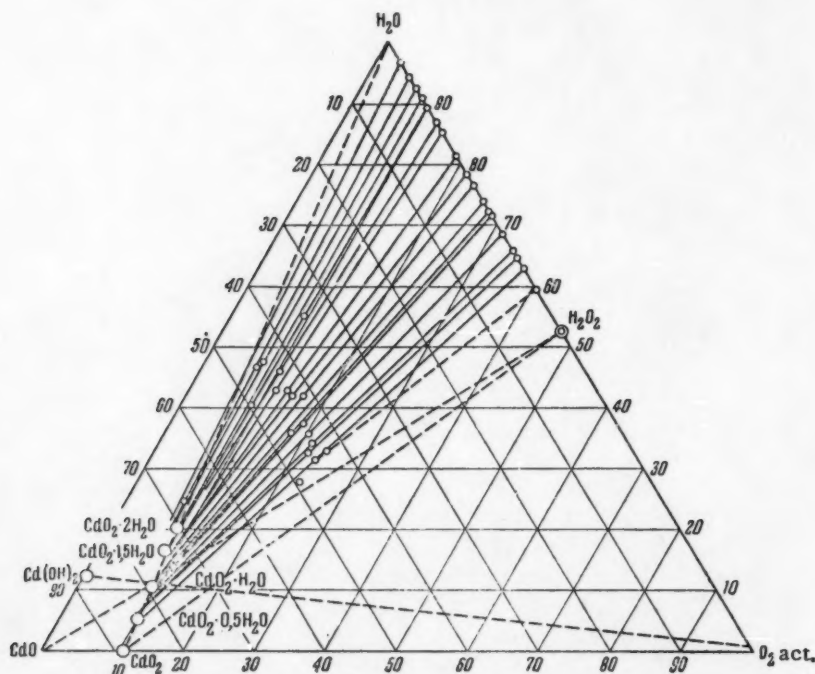


Fig. 1.  $20^\circ$  Isotherm of the ternary system  $\text{Cd}(\text{OH})_2 - \text{H}_2\text{O}_2 - \text{H}_2\text{O}$ .

The  $20^\circ$  isotherm was studied from 0.00 to 89.10% of  $\text{H}_2\text{O}_2$  in the liquid phase. The diagram in the triangular system of coordinates (Fig. 1) and the solubility curve (Fig. 2) at  $20^\circ$  indicate the presence of five solid phases:  $\text{Cd}(\text{OH})_2$ ,  $\text{CdO}_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{CdO}_2 \cdot 1.5\text{H}_2\text{O}$ ,  $\text{CdO}_2 \cdot \text{H}_2\text{O}$ ,  $\text{CdO}_2 \cdot 0.5\text{H}_2\text{O}$  (Table 1).

The solid phases were quite well formed and were readily freed from the mother liquor.

The 0° isotherm was studied over the range of 0.00 to 93.91% of  $\text{H}_2\text{O}_2$  in the liquid phase. The five solid phases found at 20° were retained at 0° in the corresponding ranges of  $\text{H}_2\text{O}_2$  concentration. The most dehydrated phase,  $\text{CdO}_2 \cdot 0.5\text{H}_2\text{O}$ , was not sufficiently stable in contact with the liquid phase at 0°. Data on the 0° isotherm are given in Table 2 and the graphs (Figs. 3 and 4).

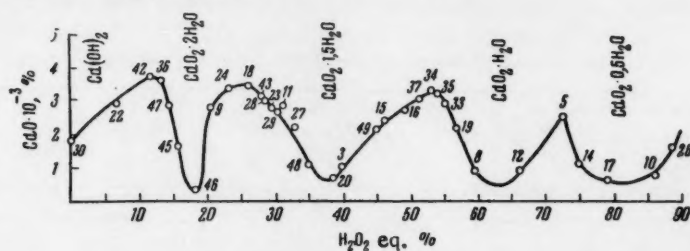


Fig. 2. Curve of the solubility of CdO in  $\text{H}_2\text{O}_2$ - $\text{H}_2\text{O}$  at 20°.

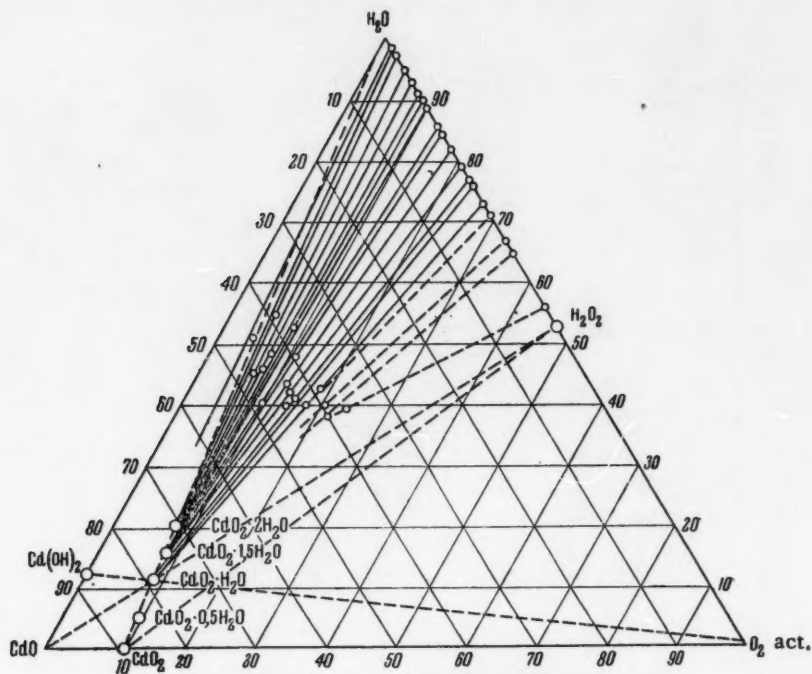


Fig. 3. 0° Isotherm of the ternary system  $\text{Cd}(\text{OH})_2$ - $\text{H}_2\text{O}_2$ - $\text{H}_2\text{O}$ .

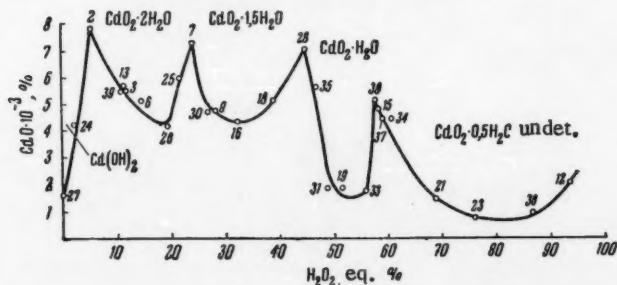


Fig. 4. Curve of the solubility of CdC in  $\text{H}_2\text{O}_2$ - $\text{H}_2\text{O}$  at 0°.

As a result of studying the system  $\text{Cd}(\text{OH})_2-\text{H}_2\text{O}_2-\text{H}_2\text{O}$  at 20 and 0° through solubility, we found five solid phases in corresponding ranges of hydrogen peroxide concentrations (Table 3). During the reaction of cadmium hydroxide with hydrogen peroxide, there arise phases of the hydrate type, whose compositions are similar to those of the solid phases found by studying the system  $\text{Zn}(\text{OH})_2-\text{H}_2\text{O}_2-\text{H}_2\text{O}$  [1]. The more detailed investigation of the solid phases of the system  $\text{Zn}(\text{OH})_2-\text{H}_2\text{O}_2-\text{H}_2\text{O}$  indicated that they contained hydroperoxide groups  $-\text{OOH}$ . It is also possible that the peroxide compounds of cadmium have a hydroperoxide structure.

TABLE 2. Data on the 0° Isotherm of the Ternary System  $\text{Cd}(\text{OH})_2-\text{H}_2\text{O}_2-\text{H}_2\text{O}$

| Expt. No. | Composition of residue, wt. % |       | Composition of liquid phase, wt. % |                        |                            | Solid phase   |
|-----------|-------------------------------|-------|------------------------------------|------------------------|----------------------------|---|
|           | act. $\text{O}_2$             | CdO   | act. $\text{O}_2$                  | $\text{H}_2\text{O}_2$ | $\text{CdO} \cdot 10^{-3}$ |   |
| 27        | —                             | —     | —                                  | —                      | 1,6                        | $\text{Cd}(\text{OH})_2$  |
| 24        | 4,51                          | 43,86 | 0,81                               | 1,72                   | 4,19                       | The same  |
| 2         | 7,46                          | 46,06 | 2,54                               | 5,40                   | 7,83                       | $\text{Cd}(\text{OH})_2 + \text{CdO}_2 \cdot 2\text{H}_2\text{O}$                   |
| 39        | —                             | —     | 4,44                               | 9,44                   | 5,29                       | $\text{CdO}_2 \cdot 2\text{H}_2\text{O}$  |
| 13        | 6,64                          | 38,48 | 5,42                               | 11,52                  | 5,63                       | The same  |
| 3         | 6,90                          | —     | 5,54                               | 11,78                  | 5,52                       | " "   |
| 5         | 7,59                          | 46,37 | 7,21                               | 15,33                  | —                          | " "   |
| 6         | 8,27                          | 42,60 | 7,34                               | 15,60                  | 5,07                       | " "   |
| 26        | 8,80                          | 42,55 | 9,35                               | 19,88                  | 4,23                       | " "   |
| 25        | 8,68                          | 44,96 | 10,06                              | 21,73                  | 5,96                       | " "   |
| 7         | 9,42                          | 37,31 | 11,21                              | 23,83                  | 7,28                       | $\text{CdO}_2 \cdot 2\text{H}_2\text{O} + \text{CdO}_2 \cdot 1,5\text{H}_2\text{O}$ |
| 30        | —                             | —     | 12,59                              | 26,76                  | 4,52                       | $\text{CdO}_2 \cdot 1,5\text{H}_2\text{O}$  |
| 9         | 21,40                         | 40,30 | 13,40                              | 28,50                  | 4,85                       | The same  |
| 20        | 11,46                         | 48,58 | 15,20                              | 32,32                  | —                          | " "   |
| 6         | 12,13                         | 39,62 | 15,45                              | 32,85                  | 4,40                       | " "   |
| 18        | 13,31                         | 43,29 | 18,31                              | 38,93                  | 5,18                       | " "   |
| 28        | 14,28                         | 43,57 | 21,18                              | 45,03                  | 7,03                       | $\text{CdO}_2 \cdot 1,5\text{H}_2\text{O} + \text{CdO}_2 \cdot \text{H}_2\text{O}$  |
| 35        | —                             | —     | 22,14                              | 47,0                   | 5,56                       | $\text{CdO}_2 \cdot \text{H}_2\text{O}$   |
| 31        | —                             | —     | 22,85                              | 48,60                  | 1,87                       | The same  |
| 10        | 15,27                         | 43,09 | 23,73                              | 50,44                  | —                          | " "   |
| 19        | 15,41                         | 45,30 | 24,27                              | 51,60                  | 1,86                       | " "   |
| 33        | —                             | —     | 26,43                              | 56,19                  | 1,76                       | " "   |
| 38        | —                             | —     | 27,44                              | 58,34                  | 5,16                       | $\text{CdO}_2 \cdot \text{H}_2\text{O} + \text{CdO}_2 \cdot 0,5\text{H}_2\text{O}$  |
| 15        | 18,05                         | 38,57 | 27,47                              | 58,40                  | 4,85                       | $\text{CdO}_2 \cdot 0,5\text{H}_2\text{O}$  |
| 37        | —                             | —     | 28,10                              | 59,74                  | 4,43                       | The same  |
| 34        | —                             | —     | 28,53                              | 60,65                  | 4,41                       | " "   |
| 22        | 17,66                         | 42,87 | 29,30                              | 62,29                  | —                          | " "   |
| 21        | 17,58                         | 42,40 | 32,41                              | 68,90                  | 1,43                       | " "   |
| 11        | 20,50                         | 39,20 | 33,32                              | 70,84                  | —                          | " "   |
| 23        | 21,54                         | 39,75 | 35,66                              | 75,81                  | 0,99                       | " "   |
| 36        | —                             | —     | 40,80                              | 86,74                  | 1,04                       | " "   |
| 12        | 24,69                         | 36,94 | 44,17                              | 93,91                  | 2,10                       | " "   |
| 14        | 27,21                         | 36,58 | 44,17                              | 93,91                  | —                          | " "   |

TABLE 3. Concentration Ranges of the Existence of the Solid Phases in the System  $\text{Cd}(\text{OH})_2-\text{H}_2\text{O}_2-\text{H}_2\text{O}$  at 20 and 0°

| Solid phase                                | $\text{H}_2\text{O}_2$ concentration range, wt. % |             |
|--|---|-------------|
|  | 20°   | 0°          |
| $\text{Cd}(\text{OH})_2$                   | 0,00—11,60  | 0,00—5,40   |
| $\text{CdO}_2 \cdot 2\text{H}_2\text{O}$   | 11,60—26,08                                       | 5,40—23,83  |
| $\text{CdO}_2 \cdot 1,5\text{H}_2\text{O}$ | 26,08—53,32                                       | 23,83—45,03 |
| $\text{CdO}_2 \cdot \text{H}_2\text{O}$    | 53,32—72,73                                       | 45,03—58,34 |
| $\text{CdO}_2 \cdot 0,5\text{H}_2\text{O}$ | 72,73—89,10                                       | 58,34—93,91 |

#### SUMMARY

1. The system  $\text{Cd}(\text{OH})_2\text{--H}_2\text{O}_2\text{--H}_2\text{O}$  at 20 and 0° was found to contain five solid phases:  $\text{Cd}(\text{OH})_2$  and four hydrated forms of cadmium peroxide:  $\text{CdO}_2 \cdot 2\text{H}_2\text{O}$ ;  $\text{CdO}_2 \cdot 1.5\text{H}_2\text{O}$ ;  $\text{CdO}_2 \cdot \text{H}_2\text{O}$ , and  $\text{CdO}_2 \cdot 0.5\text{H}_2\text{O}$ .

2. It was found that there is an analogy in the formation of peroxide compounds of the hydrate type in the systems  $\text{Cd}(\text{OH})_2\text{--H}_2\text{O}_2\text{--H}_2\text{O}$  and  $\text{Zn}(\text{OH})_2\text{--H}_2\text{O}_2\text{--H}_2\text{O}$ .

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

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# A STUDY OF THE MICROPOROUS STRUCTURE OF ACTIVATED CHARCOALS

## COMMUNICATION 1. ACTIVATED CHARCOALS FROM PHENOLALDEHYDE RESIN

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The microporous structure of activated charcoals has been attracting the attention of investigators for a long time now. What progress has been made in understanding the problem has come mainly from x-ray studies on carbonaceous materials resulting from the carbonization of organic matter, as well as on actual activated charcoals [1-7].

The most widespread interpretation of the x-ray structure data is as follows. Carbon blacks, carbonized organic materials, and activated charcoals all consist of assemblies of graphite-like "crystallites," the lattice parameters and dimensions of which are not essentially different, as long as the crystallites are formed at a temperature which does exceed 1000°. The crystallites have a laminar lattice. In each crystallite, the carbon atoms form plane, two-dimensional, hexagonal grids, but, as distinguished from graphite crystals, with occasional orientation of the plane grids around the normal to the layers.

If the temperature of formation of the crystallites is not very high, the free valences of the carbon atoms at the grid edges, lying on the lateral boundaries of the crystallites, are saturated by uniting with organic radicals, which bind the carbon grids of neighboring "crystallites" together to form a space polymer carbon skeleton [8]. If the heat treatment temperature is raised, the radicals are decomposed, and their molecular weight is reduced down to the point where they become simply the radicals of elementary hydrogen and oxygen, bound to the carbon atoms on the lateral boundaries of the crystallites.

Since the inter-planar space between the carbon grids in the crystallites is inaccessible to physically adsorbed molecules, the fundamental question that has to be considered, when we are talking about the microporous structure of activated charcoal, is how the crystallites are packed in the carbonaceous material, and how some parts of their external surface become accessible to molecules, so that they can be absorbed. However, all considerations of this sort have some rather uncertain features, owing to the fact that x-ray methods of analysis are best suited to telling whether or not there is ordered carbon in the materials under investigation. This, then, leaves the question open as to whether or not there may be a more or less large quantity of amorphous carbon in the initial carbonization products of organic matter, and, hence, in activated charcoals.

The activation of carbonized materials by gaseous substances is usually accompanied by a burn-up amounting to about 50%. It is obvious, that in the process about one half by weight, of the more reactive constituents of the charcoal is burned out. This could be the amorphous part, individual crystallites [3, 5], or part of the carbon grids in the crystallites [9]. In the first cast, the micropores formed could have a completely arbitrary form. If the things that are burned out are whole crystallites, or some of the carbon grids in the crystallites, the micropores in the charcoal ought to have a form approximating a plane crack having dimensions of molecular order. Along with macro- and medium sized pores, formed by other mechanisms, the charcoal that comes out of the activation process will contain a substantial volume of micropores, as compared with the initial carbonized material, and this is what determines the adsorbtional properties of the activated charcoals [10].

The precise nature of the microporous structure of activated charcoals is a question that is far from being solved. In our studies, we propose, in addition to the usual methods of x-ray structure analysis, to develop, as widely as possible, detailed adsorbent methods of analysis. This is based on the idea that since the micropores of the activated charcoals are of dimensions comparable to the molecules being adsorbed, the largest amount of information will be gathered about the micropores themselves by varying the dimensions and form of the molecules to be adsorbed over the widest possible range. To solve this problem, we are paying special attention to the study of how microporous structure of the activated charcoals changes with activation, heat treatment, or partial filling up with other previously adsorbed materials.

The subject of study in this first communication is the change in the microporous structure of activated charcoal resulting from heat treatment over a wide range of temperatures.

## EXPERIMENTAL

1. The activated charcoal chosen for experimental study was one made from phenolaldehyde resin. The method of preparation has already been described [11, 12]. The product obtained from carbonizing the resin was activated with carbonic acid gas in a rotating quartz retort at 950° to about 50% burnup. The ash from the activated charcoal, which came to about 0.05%, was found from x-ray data to be due principally to contamination with  $\text{SiO}_2$  from the quartz retort. This activated charcoal belongs to series "A," and it was given the designation A-950.

Samples of the A-950 charcoal were heat treated at temperatures of 1750°, 2000°, and 2300° in an atmosphere of nitrogen in a laboratory furnace with a tubular graphite heating element. The charcoal samples were placed in cylindrical graphite vessels with screwed-on graphite covers. The temperature was raised at a rate of 70° per minute, and was held constant at the desired value to within  $\pm 25^\circ$  for 45 min. The rate of cooling in a stream of nitrogen, passed through the tubular graphite heating element, did not differ materially from 80° per minute. The resulting charcoal samples were given the designations A-1750, A-2000, and A-2300.

The heat treatment of the A-950 sample at a temperature of 3000° was carried out by I. V. Uspenskii in a type RS-100 electric resistance furnace. Large cylindrical graphite crucibles with screwed-on covers were loaded between the electrodes, and served as the heating element. Samples of the various activated charcoal series in hermetically sealed graphite tubes were placed in one of the large crucibles, and covered with lamp black previously heat treated at 3000°. The heating element was also covered with a layer of lamp black 20 cm thick. The temperature was raised at a mean rate of about 120° per minute. Constant temperature was maintained for 45 min. The resulting charcoal sample was called A-3000.

The heat treatment produced a marked reduction in the weight of the charcoal, amounting to 3.21% at 1750°, 3.50% at 2000°, 5.53% at 2300°, and 5.57% at 3000°. This shows that the initial A-950 activated charcoal was not pure carbon.

2. The x-ray diagrams of the charcoal samples were taken by the Debye-Scherrer method in a VRS-3 camera with a diameter of 143.5 mm, using filtered copper radiation. The exposure time for a single picture extended up to 25-30 hr. The first experiments at long exposures showed strong quartz lines, due to traces of contamination by  $\text{SiO}_2$  from the quartz retort. These disappeared after the charcoal was treated with HF and HCl, which produced no observable change in the lattice constants or the dimensions of the crystallites. The microphotographs of the purified charcoal samples are given in Fig. 1. The x-ray diagrams of the initial A-950 activated charcoal show the diffuse bands (002) and (10), along with intense scattering inside the (002) ring, which increases toward the small angle side. Increasing the temperature at which the charcoal was heat treated reduces the half width and increases the intensity of the lines (002), (10), (004), and (11). However, the A-950 activated charcoal is not graphitized, and it is only after it has been heated to 3000° that the x-ray diagrams show sharp (101) and (112) lines, which indicate that heterogeneous graphitization has taken place. If the heat treatment temperature has been held constant for 45 min, the amount of actual graphite in the A-3000 sample amounts to about 20%.

The dimensions of the carbon crystallites were determined from the half widths of the lines (hk) and (00l) by Warren's formulas [13]:

$$L_c = \frac{0.90\lambda}{b_{00l} \cos \theta} \quad (1)$$

$$L_a = \frac{1,84 \lambda}{b_{hk} \cos \theta} \quad (2)$$

where  $\lambda$  is the wavelength of the x-rays, and  $b$  and  $\theta$  are respectively the angular half width and the angle of diffraction of the lines (00l) and (hk).

In addition to the crystal parameters  $L_c$  and  $L_a$ , we determined the x-ray density of the crystallites,  $\rho$ , in mass per unit volume of the elementary crystallite cell. The value of  $\rho$  was calculated from the formula:

$$\rho = \frac{z Am}{abc} = \frac{7,627}{d_{002}} \text{ gm/cm}^3 \quad (3)$$

where  $z = 4$  is the number of carbon atoms in the elementary cell,  $A = 12$  is the atomic weight of carbon,  $m = 1,66 \cdot 10^{-24}$  gm is the mass of the hydrogen atom,  $a$  and  $b$  are the constants of the crystal lattice of graphite for the elementary plane ( $a = b = 2,456 \text{ \AA}$ ) and  $c = 2d_{002}$  is the dimension of the elementary cell along the  $c$  axis, equal to twice the interplanar distance  $d_{002}$  in  $\text{\AA}$ . The interplanar distance is determined from the position of the (002) line in the microphotograms.

The basic data from the x-ray structure analysis of the charcoal samples is given in Table 1. The parameters  $L_c$  and  $L_a$  were measured to an accuracy of  $\pm 0,5 \text{ \AA}$ .

TABLE 1. Data from the X-ray Study of Charcoals

| Charcoal | $L_c, \text{ \AA}$ |          | $L_a, \text{ \AA}$ |         | $d_{002}, \text{ \AA}$ | $\rho, \text{ gm/cm}^3$ |
|----------|--------------------|----------|--------------------|---------|------------------------|-------------------------|
|          | at (002)           | at (004) | at (10)            | at (11) |                        |                         |
| A-950    | 8                  | 8        | 21                 | 22      | 3,99                   | 1,91                    |
| A-1750   | 10                 | 11       | 31                 | 34      | 3,73                   | 2,04                    |
| A-2000   | 12                 | 13       | 39                 | 40      | 3,58                   | 2,13                    |
| A-2300   | 15                 | 15       | 43                 | 45      | 3,48                   | 2,19                    |
| A-3000   | 22                 | 23       | 51                 | 52      | 3,40                   | 2,24                    |

Heat treatment of the initial A-950 activated charcoal at  $3000^\circ$  increases the parameter  $L_c$ , which brings about a change in the coherent scattering region for x-rays, corresponding to a change in crystallite height from 8 to  $22,5 \text{ \AA}$ . The parameter  $L_a$ , the diameter of the planar carbon layers, is increased from  $21,5$  to  $51,5 \text{ \AA}$ . The number of carbon layers (plane six-membered grids of carbon atoms) in the packet, i.e., the crystallite, is increased from 3, for the initial A-950 charcoal, to 7, for the sample of A-3000 charcoal.

Raising the temperature at which the A-950 activated charcoal is heat treated reduces the interplanar distance  $d_{002}$ , at the same time that it changes the parameters  $L_c$  and  $L_a$ . This means a more dense packing of the carbon atoms in the crystallites, with an increase in the x-ray density from  $1,91$  to  $2,24 \text{ gm/cm}^3$ .

3. To determine the characteristic adsorbtional properties, and find out something about the elements of the porous structure of the charcoal samples, adsorbtion isotherms were taken at  $20^\circ$  for the vapors of benzene, cyclohexane, and water, over a wide range of equilibrium relative pressures, using the vacuum sorbed weight method.

Figures 2 and 3 show the adsorbtion isotherms of benzene and cyclohexane vapor on the charcoal samples under study. The curves show the adsorbtional properties of the charcoals in the middle and high ranges of equilibrium relative pressures. The higher the temperature of the heat treatment to which the initial A-950 charcoal has been subjected, the greater the reduction in the adsorbtivity of the resulting samples. The A-2300 charcoal adsorbs benzene vapor rather markedly, but the cyclohexane is adsorbed only at high relative pressures. The general form of the sorbtion isotherms gives evidence for the existence of a small volume of medium sized pores in the charcoal samples studied.

Figure 4 shows the sorbtion isotherms of water vapor. With increasing heat treatment temperature, the same general behavior is observed as with organic vapors, namely, a reduction in the limiting sorbtion values. Going from charcoal A-950 to charcoal A-2300 there is a displacement of the rapidly rising part of the curve toward the

high relative pressure region. Curves A-1750 and A-2000 show characteristic kinks, which, apparently, mean that the surface of the charcoal is becoming more uniform.

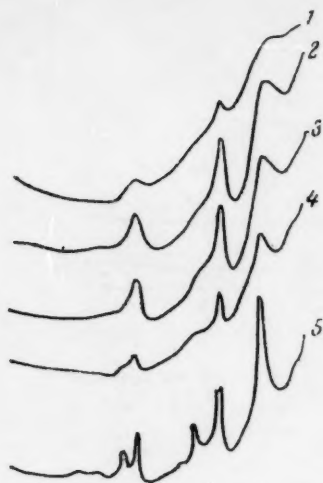


Fig. 1. Charcoal microphotographs. 1) A-950; 2) A-1750; 3) A-2000; 4) A-2300; 5) A-3000.

Table 2 gives the limiting sorption values, and the limiting sorption volumes, calculated on the assumption of normal density of the adsorbed substance in the liquid state in the pores of the charcoal.

The difference in the values of the limiting sorption volumes on the charcoal samples for benzene and cyclohexane is due, fundamentally, to the difference in sorption values at the points of incipient hysteresis, i.e., to the difference in volume of the micropores, as determined from the respective sorption isotherms of benzene and cyclohexane vapor. The special aspects of filling up the pores of activated charcoal, which are encountered in the limiting sorption of water vapor, have already been discussed [14].

The isotherm equation, given by the potential theory of adsorption for adsorbents of the first structural type [15, 16], was applied to the experimental isotherms of benzene and cyclohexane vapor. This equation may be written in the form:

$$a = a'_0 e^{-B \frac{T^*}{\beta^2} (\lg p_s/p)^2} \quad (4)$$

where the limiting adsorption value,  $a'_0$  corresponds to complete filling of the limiting volume of the adsorbent space  $W_0$ .

$$a'_0 = \frac{W_0}{v} \quad (5)$$

Here  $v$  designates the volume in 1 mM of matter in the adsorbed state.

Figure 5 shows the adsorption isotherm of benzene vapor on A-1750 as an example of the linear form of the curve corresponding to Eq. (4). The curves of the other charcoal samples have the same form both for benzene vapor and cyclohexane vapor. In the present case, we are dealing with activated charcoals of a mixed structural type, containing two varieties of micropore. In the micropores of the first structural type, corresponding to the limiting adsorption value  $a'_0$ , the effect of raising the adsorbent potentials is observed. In the larger micropores of the second structural type, which are characterized by the limiting adsorption value  $a''_0$ , this effect is practically absent. In the familiar approximation,

$$a'_0 + a''_0 = a^0 \quad (6)$$

where  $a^0$  is the value of adsorption corresponding to the point of incipient hysteresis in the capillary condensation of a vapor in the medium sized pores. In the curve of Fig. 5, the vertical intercept of the straight line gives the equilibrium pressure  $(p/p_s)_0 = 0.175$  for the point of incipient hysteresis [17, 18]. The adsorption on the surface of micropores of the second structural type, which rises rapidly in the region of higher equilibrium pressures, is the fundamental reason why the region of applicability of Eq. (4) is compressed toward the high pressure side.

Table 3 gives the constants of the adsorption isotherm Eq. (4), along with the values of the affine coefficients  $\beta$ . In calculating the limiting sorption volumes,  $W_0$ , from Eq. (5), the value  $v = 0.0888 \text{ cm}^3/\text{mM}$  was taken for benzene, and the value  $v = 0.108 \text{ cm}^3/\text{mM}$  was taken for cyclohexane, corresponding to the densities in volume of the liquid phases.

The limiting volumes of the adsorption space are greater for benzene than for cyclohexane. This difference is practically absent in the initial A-950 active charcoal [19], but it becomes considerable for samples heated to high temperatures. The systematic increase in the constant  $B$  as the charcoal heat treatment temperature is raised gives some qualitative evidence for an increase in the dimensions of the micropores, which have a very definite importance for the enhanced adsorption potential effect.

The volumes of the different varieties of pores in the charcoal samples under study were evaluated from the sorption isotherms of benzene vapor. The volumes of the micro- and medium sized pores were determined by the usual method from the sorption volumes at the points of incipient hysteresis ( $v_{ml}$ ), and from the differences between

the limiting sorption volumes and  $v_{mi}$  [10]. On the basis of Eq. (6), the total micropore volume was divided between micropores of the first and second structural type. Throughout all the pore volume calculations, the value  $\underline{v} = 0,0888$   $\text{cm}^3/\text{mM}$  was assumed for benzene. The results are given in Table 4.

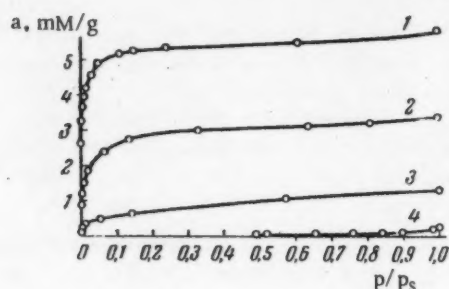


Fig. 2. Adsorption isotherms of benzene vapor at 20° for the charcoals. 1) A-950; 2) A-1750; 3) A-2000; 4) A-2300.

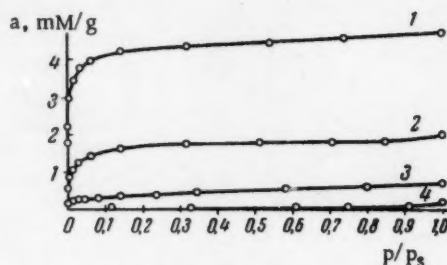


Fig. 3. Adsorption isotherms of cyclohexane vapor at 20° for the charcoals. 1) A-950; 2) A-1750; 3) A-2000; 4) A-2300.

TABLE 2. Limiting Sorption Values and Sorption Volumes

| Char-coal | $\text{C}_6\text{H}_6$ |                                 | $\text{C}_6\text{H}_{12}$ |                                 | $\text{H}_2\text{O}$ |                                 |
|-----------|------------------------|---------------------------------|---------------------------|---------------------------------|----------------------|---------------------------------|
|           | $a_s$<br>mM/g          | $v_s$<br>$\text{cm}^3/\text{g}$ | $a_s$<br>mM/g             | $v_s$<br>$\text{cm}^3/\text{g}$ | $a_s$<br>mM/g        | $v_s$<br>$\text{cm}^3/\text{g}$ |
| A-950     | 5,84                   | 0,519                           | 4,79                      | 0,518                           | 27,1                 | 0,488                           |
| A-1750    | 3,36                   | 0,299                           | 2,03                      | 0,240                           | 16,8                 | 0,302                           |
| A-2000    | 1,27                   | 0,113                           | 0,711                     | 0,077                           | 4,45                 | 0,080                           |
| A-2300    | 0,198                  | 0,018                           | 0,165                     | 0,018                           | 0,189                | 0,0034                          |
| A-3000    | 0,11                   | 0,010                           | —                         | —                               | —                    | —                               |

TABLE 3. Constants of the Adsorption Isotherm Equation

| Vapor                     | Char-coal | $a_0^*$<br>mM/g | $W_0^*$<br>$\text{cm}^3/\text{g}$ | $B \cdot 10^4$ | $\beta$ | Range of applicability<br>$p/p_s$     |
|---------------------------|-----------|-----------------|-----------------------------------|----------------|---------|---------------------------------------|
| $\text{C}_6\text{H}_6$    | A- 950    | 4,62            | 0,410                             | 0,773          | 1,00    | $1,6 \cdot 10^{-6} - 2 \cdot 10^{-3}$ |
|                           | A-1750    | 1,59            | 0,141                             | 0,873          | 1,00    | $5 \cdot 10^{-6} - 2 \cdot 10^{-3}$   |
|                           | A-2000    | 0,57            | 0,051                             | 2,07           | 1,00    | $2 \cdot 10^{-4} - 4 \cdot 10^{-2}$   |
| $\text{C}_6\text{H}_{12}$ | A- 950    | 3,80            | 0,410                             | 0,773          | 1,00    | $7 \cdot 10^{-6} - 2 \cdot 10^{-3}$   |
|                           | A-1750    | 0,91            | 0,098                             | 0,873          | 0,995   | $3 \cdot 10^{-6} - 7 \cdot 10^{-4}$   |
|                           | A-2000    | 0,30            | 0,033                             | 2,07           | 1,02    | $1,5 \cdot 10^{-6} - 1 \cdot 10^{-2}$ |

TABLE 4. Volumes of Different Varieties of Charcoal Pores in  $\text{cm}^3/\text{gm}$

| Charcoal | $v_{mi}$ | Components of $v_{mi}$ |            | $v_p$ | $v_s$ |
|----------|----------|------------------------|------------|-------|-------|
|          |          | $v'_{mi}$              | $v''_{mi}$ |       |       |
| A- 950   | 0,474    | 0,410                  | 0,064      | 0,045 | 0,519 |
| A-1750   | 0,253    | 0,141                  | 0,112      | 0,046 | 0,299 |
| A-2000   | 0,060    | 0,051                  | 0,009      | 0,053 | 0,113 |
| A-2300   | 0,002    |                        |            | 0,016 | 0,018 |
| A-3000   | 0,000    |                        |            | 0,010 | 0,010 |

Heat treatment of the A-950 charcoal produces a marked reduction in the total micropore volume, in particular at temperatures approaching 2000°. The micropores of the first structural type show an even more pronounced drop in volume, initially on account of some increase in volume of the micropores of the second structural type. Up to temperatures of 2000°, the volume of the medium sized pores remains practically unchanged, but with further increase in temperature, this volume is substantially reduced, and for A-2300 and A-3000 charcoals it is practically the determining factor in the limiting sorption capacity.

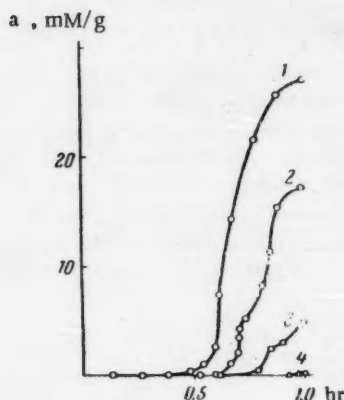


Fig. 4. Sorption isotherms of water vapor at 20° for the charcoals. 1) A-950; 2) A-1750; 3) A-2000; 4) A-2300.

TABLE 5. Constants in the Adsorption Isotherm Equation of Water Vapor

| Char-coal | $a_0$ , mm/g | $c$  |
|-----------|--------------|------|
| A-950     | 0,153        | 1,58 |
| A-1750    | 0,095        | 1,38 |
| A-2000    | 0,061        | 1,24 |
| A-2300    | 0,0028       | 1,01 |

electrolytes). The usual titrimetric and colorimetric methods were used to analyze the solutions. The experimental results are given in Tables 6 and 7.

Heat treatment of the A-950 charcoal lowers the amount of all the substances under investigation that was absorbed, as a result of the reduction in the specific surface of the micropores, along with a reduction in the accessibility of the micropores to large molecules such as methylene blue, and submicroscopic particles such as Congo red. Thus, the A-1750 charcoal, which still shows considerable adsorptivity for dissolved substances, including methylene blue, practically fails to adsorb Congo red.

Apparently, this effect has nothing to do with a reduction in dimensions of the micropores (the increase in the constant B in Table 3 provides evidence of increasing micropore dimensions on going from A-950 to A-2000 charcoal), but rather is a matter of narrowing down the entrances to the micropores, which causes an ultraporosity effect to appear. Confirmation of this assumption is furnished by the higher relative values of adsorption shown by organic acids of higher molecular weight (butyric and caproic), as well as by phenol, when they are adsorbed on A-2000 charcoal, and to some extent on A-1750, as compared with the first members of the homologous acid series.

The experiments on the adsorption of electrolytes (Table 7), show that the chemical nature, of the charcoal surface is not changed by heat treatment. However, heat treating the initial activated charcoal has a particularly strong effect on the ability of the samples to adsorb oxygen chemically, with the formation of surface oxides having a basic character, which give the charcoal the property of anion exchange (HCl adsorption and hydrolytic NaCl adsorption). Since these surface oxides are primordial adsorption centers in the adsorption of water vapor [21], it is

In the light of the concepts already developed [20], the adsorption of water vapor in the initial region of the isotherm, including the characteristic rise in the adsorption branch, is due to the presence of primordial adsorption centers on the surface of the charcoal, namely, the charcoal surface oxides. In this case, the adsorption isotherm equation takes the form:

$$a = \frac{a_0 c h}{1 - c h} \quad (7)$$

where  $a_0$  is the number of primordial adsorption centers in mm/gm,  $c$  is a constant, and  $h$  is the equilibrium relative pressure. Table 5 gives the values of the constants in Eq. (7) as determined by experiment.

The change in the values of the constants provides evidence for a considerable reduction in the number of primordial adsorption centers in the charcoal samples accompanying an increase in the temperature at which the initial A-950 charcoal is heat treated. The change in the constants also shows that the region in which the adsorption branch of the isotherm starts to rise rapidly is displaced toward the high relative pressure side [21].

4. To learn something about the characteristic adsorbtional properties, the porous structure, and the nature of the surface of the samples, measurements were made on the amount of adsorption from aqueous solutions of representatives of a number of normal, monobasic, fatty acids; phenol; some dyes, and strong electrolytes. The experimental conditions were not materially different from those described previously [22]. The initial concentration of the solutions was 0.01 M or N (for methylene blue 0.15%, and for Congo red 0.05%), the volume of the solution was 25 cm<sup>3</sup>, the amount of charcoal added was 0.1 gm (0.25 gm for HCl, 0.5 gm for NaCl, and 1 gram for NaOH), and the time of shaking in glass cylinders with ground in stoppers at 20-22° was 24 hr (4 hr for strong elec-

natural that there would be a qualitative correspondence between the change in  $a_0$  and the change in electrolyte adsorption values as the heat treatment temperature of the charcoal is raised. It should be noted, that with heat treated charcoal samples, the values of  $a_0$  are apt to be a little exaggerated, as a result of neglecting the adsorption of water vapor on the homogeneous surface, which has nothing to do with the presence of primordial adsorption centers.

## DISCUSSION OF RESULTS

1. From the data on the crystallite parameters  $L_c$ ,  $L_a$  and  $\rho$ , one can calculate the integrated external surface of the crystallites in one gram of charcoal, considering them to be cylinders of diameter  $L_a$  and altitude  $L_c$ . A calculation of this sort is based on the assumption that the charcoal samples consist exclusively of crystallites, and there is no amorphous carbon in them. In this case, the integrated lateral surface of the cylindrical crystallites in one gram of charcoal,  $S_L$ , will be given by the expression:

$$S_B = \frac{4}{L_a \rho} \text{ cm}^2/\text{g} \quad (8)$$

and the integrated surface of the bases (cross sectional areas) of the cylindrical crystallites will be equal to:

$$S_T = \frac{2}{L_c \rho} \text{ cm}^2/\text{g} \quad (9)$$

For the total integrated surface of the crystallites we obtain:

$$S = S_B + S_T \quad (10)$$

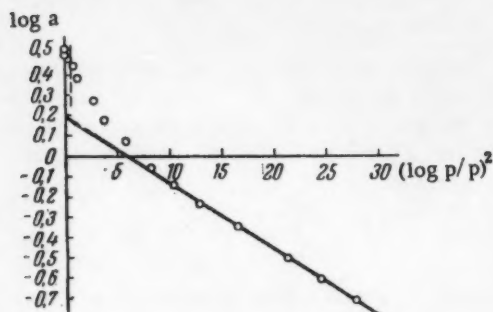


Fig. 5. Adsorption isotherm of benzene vapor at 20° for A-1750 charcoal. Linear form corresponding with Eq. (4).

TABLE 6. Values of the Adsorption of Dissolved Substances

| Adsorbed substance | a, mM/g |        |        | Relative values of adsorption |        |        |
|--------------------|---------|--------|--------|-------------------------------|--------|--------|
|                    | A-950   | A-1750 | A-2000 | A-950                         | A-1750 | A-2000 |
| Formic acid        | 0,555   | 0,218  | 0,050  | 1,00                          | 0,39   | 0,090  |
| Acetic acid        | 0,805   | 0,315  | 0,075  | 1,00                          | 0,39   | 0,093  |
| Propionic acid     | 1,297   | 0,488  | 0,118  | 1,00                          | 0,38   | 0,091  |
| Butyric acid       | 1,705   | 0,697  | 0,190  | 1,00                          | 0,41   | 0,111  |
| Caproic acid       | 2,367   | 1,332  | 0,400  | 1,00                          | 0,56   | 0,169  |
| Phenol             | 2,035   | 1,280  | 0,285  | 1,00                          | 0,63   | 0,140  |
| Methylene blue     | 1,015   | 0,243  | 0,055  | 1,00                          | 0,24   | 0,054  |
| Congo red          | 0,088   | 0,0044 | 0,000  | 1,00                          | 0,05   | 0,00   |

TABLE 7. Adsorption of Electrolytes from Water Solution in mE/gm

| Charcoal | HCl   |       | NaOH   | NaCl  |       |
|----------|-------|-------|--------|-------|-------|
|          | H+    | Cl-   |        | Cl-   | OH-   |
| A- 950   | 0,307 | 0,303 | 0,001  | 0,034 | 0,030 |
| A-1750   | 0,079 | 0,075 | 0,000  | 0,013 | 0,013 |
| A-2000   | 0,008 | 0,007 | -0,001 | 0,000 | 0,001 |
| A-2300   | 0     | 0     | 0,001  |       | 0,000 |

In Table 8, the calculated x-ray surfaces of the crystallites are compared with those found from the adsorption isotherm equations of Brunauer, Emmett, and Teller [23], and Langmuir.

TABLE 8. Specific Surfaces in  $\text{m}^2/\text{gm}$

| Charcoal | X-ray surfaces |       |      | BET, $\text{C}_6\text{H}_6$ |      | Langmuir, $\text{C}_6\text{H}_6$ |      | BET, $\text{C}_6\text{H}_{12}$ |     |
|----------|----------------|-------|------|-----------------------------|------|----------------------------------|------|--------------------------------|-----|
|          | $S_B$          | $S_T$ | $S$  | $a_m$                       | $S$  | $a_m$                            | $S$  | $a_m$                          | $S$ |
| A-950    | 970            | 1310  | 2280 | 4,58                        | 1130 | 5,12                             | 1270 | 3,71                           | 850 |
| A-1750   | 610            | 940   | 1550 | 2,48                        | 610  | 2,67                             | 660  | 1,45                           | 330 |
| A-2000   | 480            | 750   | 1230 | 0,514                       | 130  | 0,483                            | 119  | 0,289                          | 66  |
| A-2300   | 420            | 610   | 1030 | 0,024                       | 6    |                                  |      | 0,013                          | 3   |
| A-3000   | 350            | 390   | 740  |                             |      |                                  |      |                                |     |

For the molecular areas of benzene and cyclohexane in continuous monomolecular layers, we took the values  $41 \text{ \AA}^2$  and  $38 \text{ \AA}^2$  respectively, which are supported experimentally and theoretically by the structural formula of the molecules [24]. The quantity  $a_m \text{ mM/gm}$  designates the value of adsorption, corresponding to the formation of continuous monomolecular layers.

In contrast to reference [6], the x-ray surfaces of the crystallites very considerably exceed the values obtained by adsorption methods, even for the well activated initial A-950 charcoal. As far as the adsorption surfaces are concerned, their formal significance should be noted. The constant  $c$  in the BET equation changes, in the case of benzene, from 2190 for A-950 charcoal, to 41 for A-2300 charcoal, which cannot be justified theoretically. The BET adsorption isotherm equation is applicable over a narrow range of equilibrium relative pressures, and the same thing can be said about Langmuir's equation. The values of  $a_m$  found are, in general, close to the adsorption values for the points of incipient hysteresis, which correspond to volume filling of the micropores.

2. It is possible to make only the most preliminary sort of attempt at reconciling the x-ray and adsorption data from the microporosity of the first structural type shown by the initial A-950 charcoal. Since, on activating the charcoals over a wide range of burn-ups, the dimensions of the crystallites do not change appreciably, leaving open the question of whether or not there are substantial amounts of amorphous carbon present in the initial carbonized material, it may be considered fairly probable that whole crystallites are burned out in the activation process. As a result, fissure-like pores may be formed in the mass of practically inactive charcoal, the dimensions of which correspond to the burn out of one crystallite, two neighboring crystallites, etc.

From the x-ray structure data, the mean height of the crystallites in the A-950 charcoal is  $L = 8 \pm 0,5 \text{ \AA}$ . If we start with the experimentally and theoretically well founded molecular areas of  $41 \text{ \AA}^2$  for benzene, and  $38 \text{ \AA}^2$  for cyclohexane, the heights,  $l$ , of the molecules may be determined from the molar volumes  $88,8 \text{ cm}^3/\text{M}$  for benzene, and  $108,0 \text{ cm}^3/\text{M}$  for cyclohexane, both in the volume liquid phase, since they are only slightly compressible. Then we obtain for the adsorbed benzene molecule  $2l_b = 3,60 \text{ \AA}$ , and correspondingly, for the cyclohexane molecule  $l_c = 4,72 \text{ \AA}$ . The reliability of these values is illustrated by the good agreement between the value of  $l_b$  and the data obtained by other methods [25].

The limiting values of adsorption for micropores of the first structural type, from the data of Table 3, are, for benzene,  $a_0^b = 4,62 \text{ mM/gm}$ , and for cyclohexane,  $a_0^c = 3,80 \text{ mM/gm}$ . A fissure-like pore, caused by the burn out of one crystallite, and thus having a height  $L = 8 \pm 0,5 \text{ \AA}$ , is big enough to hold two layers of benzene molecules ( $2l_b = 7,20 \text{ \AA}$ ), and one layer of cyclohexane molecules ( $l_c = 4,72 \text{ \AA}$ ). In this case, the ratio of the number of benzene and cyclohexane molecules adsorbed in the pores at the limit ought to be about 2, instead of  $a_0^b/a_0^c = 4,62/3,80 = 1,21$ , as given by the experimental data. Hence, the concept of micropores with a height equal to the height of a burned out crystallite cannot be reconciled with the experiment.

Let us then assume that along with the fissure-like micropores, corresponding to the burn out of just one crystallite for each micropore, giving a height  $L = 8 \text{ \AA}$  ("unitary" micropores), "double" height micropores are formed by burning out two crystallites lying on top of one another. Then the height of the double micropores will be  $L = 20 \text{ \AA}$ , or a little more.\* Double micropores of this sort can hold five layers of benzene molecules ( $5l_b = 18,0 \text{ \AA}$ ), and four

\* Actually, the bases of adjacent crystallites are probably inclined at a small angle to one another, because otherwise the experimental parameter  $L_c$  would turn out to be two or more times as big as it is. The distance between the crystallites cannot be less than  $d_{002} = 4 \text{ \AA}$  (Table 1). Therefore  $L = 16 + 4 = 20 \text{ \AA}$ .

layers of cyclohexane molecules ( $4 l_c = 18.7 \text{ \AA}$ ). The assumptions that we have just formulated provide an approximate model of the microporous structure of an activated charcoal, consisting of an assembly of two different kinds of plane fissure-like pores, each having a different height. The approximation consists of not having taken any account of the depth or width of the fissures, which is what limits the number of adsorbed molecules that can be got into the pores. In other words, the ratio of the wall area of one pore to the molecular area of the adsorbed substance is considered to be rather large. In fact, it is only equal to 11 or 12.

Let  $s$  represent the specific surface of the micropores, i.e., the integrated surface of all the pairs of walls of all the pores per unit mass of charcoal. Let the fraction  $\alpha$  of this surface be in unitary pores, and the fraction  $1 - \alpha$  be in double height pores. If the height of a unitary pore is such as to accommodate  $n_1'$  molecules of one vapor, and  $n_2'$  molecules of a second vapor, while the double pores accommodate  $n_1''$  and  $n_2''$  molecules respectively, we will have the following equations for the number of molecules of the first vapor,  $a_0'$ , and the number of molecules of the second vapor,  $a_0''$ , adsorbed in the limit: For the first vapor

$$\frac{\alpha s}{2\omega_1} n_1' + \frac{(1-\alpha)s}{2\omega_1} n_1'' = a_0' \quad (11)$$

and for the second vapor

$$\frac{\alpha s}{2\omega_2} n_2' + \frac{(1-\alpha)s}{2\omega_2} n_2'' = a_0'' \quad (12)$$

in which  $\omega_1$  and  $\omega_2$  are the molecular areas of the adsorbed molecules. Solving these equations, we obtain:

$$\alpha = \frac{An_2'' - n_1''}{(An_2'' - n_1'') - (An_2' - n_1')} \quad (13)$$

where  $A$  is the ratio:

$$A = \frac{a_0'\omega_1}{a_0''\omega_2} \quad (14)$$

and

$$s = \frac{2a_0'\omega_1}{\alpha n_1' + (1-\alpha)n_1''} \quad (15)$$

In our case,  $a_0' = a_0^b$ , and  $a_0'' = a_0^c$  are expressed in mM/gm. Then, for 1 mM of material in a monolayer,  $\omega_1 = 247 \text{ m}^2/\text{gm}$  ( $\omega = 41 \text{ \AA}^2$ ), and  $\omega_2 = 229 \text{ m}^2/\text{gm}$  ( $\omega = 39 \text{ \AA}^2$ ).

From Eqs. (13) and (15), we obtain  $\alpha = 0.256$ , and  $s = 568 \text{ m}^2/\text{gm}$  for A-950 charcoal. Thus, the activation process forms unitary micropores which occupy 26% of the surface, and double micropores which occupy 74%. The preponderance of double pores is possibly due to an incipient reaction between the activating agent and the material between the crystallites, as a result of which two adjacent crystallites burn out.

This approximate model of the micropores of the first structural type, which we have just been discussing, is, in general, found to be in agreement both with x-ray structure data, and with adsorption measurements. It leads to a reasonable value for the specific surface of the base part of the micropores of the charcoal, and to pore dimensions which insure the accessibility of a large part of them to large dye molecules. The calculations that have been made are only of the nature of an estimate, and will be refined in subsequent papers, where additional experimental data will be presented in an effort to explain the microporous structure of activated charcoals after they have been heat treated at high temperature. We shall also return to a discussion and analysis of the basic experimental data presented in the present paper.

In conclusion, the authors are conscious of the debt of gratitude to be expressed to D. N. Strazhesko for his cooperation in carrying out the experiments on the adsorption of dissolved substances, and to S. G. Tolkachev and I. V. Uspenskii for carrying out the high temperature heat treatment of the charcoal.

#### SUMMARY

1. X-ray structure and adsorption studies have been made on a series of charcoal samples prepared by heat treatment of activated charcoal made from phenolaldehyde resin at temperatures up to  $3000^\circ$ .

2. A preliminary attempt has been made to investigate the formation of the fissure-like pores in the activated charcoal resulting from burn-out during activation of the elementary crystallites, by bringing the pore parameters, which reflect the x-ray structure data, into agreement with the fundamental results of the adsorption measurements.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

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## A STUDY OF THE MICROPOROUS STRUCTURE OF ACTIVATED CHARCOALS

### COMMUNICATION 2. ACTIVATED CHARCOALS FROM POLYVINYLIDENE CHLORIDE

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One of the promising ways of finding out something about the microporous structure of activated charcoals is to study how it changes, using a combination of physical, physical chemical, and chemical methods for the purpose. In the preceding investigation [1], the change was brought about by high temperature heat treatment of activated charcoal made from phenolaldehyde resin. The present paper gives the results of similar experiments on activated charcoal made from polyvinylidene chloride. The microporous structure of this charcoal is produced by thermal decomposition of the molded polymer, with evolution of HCl, and not by activation with gaseous agents, in the course of which a substantial quantity of the carbon is burned out.

### EXPERIMENTAL

1. The method of preparing the activated charcoal from polyvinylidene chloride does not differ materially from the one already described [2], and was similar to the one used in [3]. Supplemental activation of the charcoal was carried out at 750° in CO<sub>2</sub> to about 10% burn-up. This final treatment did not have any substantial effect on the microporous structure of the charcoal, but it markedly improved its kinetic characteristics. The initial charcoal was designated as B-750, and the other charcoal samples of the B-series were prepared from it by heat treatment in an inert atmosphere at various temperatures.

The heat treatment of samples of B-750 charcoal at 1300, 1750, and 2300°, with the temperature held constant for 45 min, was done in an atmosphere of nitrogen in a laboratory furnace, with a tubular graphite heating element. The details of the experiments are given in [1]. The heat treatment of the B-750 charcoal at 3000°, with the temperature also held constant for 45 min, was carried out by I. V. Uspenskii in a type RS-100 electric resistance furnace, under the conditions described in [1]. The heat treatment produced a noticeable reduction in weight of the charcoal, amounting to 0.38% at 1300°, 4.00% at 1750°, 5.35% at 2300°, and 7.17% at 3000°.

2. The techniques for the x-ray structure analysis and the calculation of the carbon crystallite dimensions,  $L_c$  and  $L_a$ , the interplanar distance  $d_{002}$ , and the x-ray density of the crystallites,  $\rho$ , are given in [1]. The microphotographs of the charcoal samples are given in Fig. 1.

The x-ray diagrams of the initial B-750 charcoal show the diffuse bands (002), (10), (004), and (11) on an intense background, which becomes less on going to the succeeding charcoal samples. Increasing the heat treatment temperature of the B-750 charcoal, as in the case of A-950 [1], reduces the half width, and increases the intensity of the bands (002), (10), (004), and (11). But in contrast to A-950 charcoal, the greatest changes occur at temperatures above 1750°. A temperature of 3000° is only the beginning of graphitization, and the B-3000 x-ray diagram shows clear traces of the (101) line, which corresponds with complete graphitization.

From the band intensities, it is possible to make a semiquantitative judgment of the changes taking place in the carbonized polyvinylidenechloride as it is heat treated up as far as 3000°. The greater part of the carbonaceous material (~70%) goes through a precrystalline stage, and is starting homogeneous graphitization at 3000°. Approximately 25% of the material heated to the constant temperature of 3000° for 45 min remains in the disordered state, and is not graphitized. The B-3000 charcoal does not contain more than 5% perfect graphite.

The basic data from the x-ray structure analysis of the graphite samples is given in Table 1. The parameters  $L_c$  and  $L_a$  are determined with an accuracy of  $\pm 0.5 \text{ \AA}$ .



Fig. 1. Microphotographs of the charcoals: 1) B-750; 2) B-1300; 3) B-1750; 4) B-2300; 5) B-3000.

TABLE 1. Data from the X-ray Analysis of Charcoals

| Char-coal | $L_c, \text{\AA}$ |          | $L_a, \text{\AA}$ |         | $d_{002}, \text{\AA}$ | $\rho, \text{g/cm}^3$ |
|-----------|-------------------|----------|-------------------|---------|-----------------------|-----------------------|
|           | at (002)          | at (004) | at (10)           | at (11) |                       |                       |
| B-750     | 7                 | 8        | 21                | 23      | 3.85                  | 1.98                  |
| B-1300    | 7                 | 8        | 24                | 24      | 3.73                  | 2.05                  |
| B-1750    | 9                 | 9        | 25                | 26      | 3.52                  | 2.16                  |
| B-2300    | 10                | 10       | 38                | 40      | 3.46                  | 2.20                  |
| B-3000    | 17                | 19       | 48                | 50      | 3.40                  | 2.24                  |

As the heat treatment temperature of the initial B-750 charcoal is raised, we observe an increase in the parameter  $L_c$ , which gives the height of the crystallites, from 7.5 to 18  $\text{\AA}$ , and an increase in  $L_a$ , the diameter of the plane carbon layers, from 22 to 49  $\text{\AA}$ . The number of carbon layers in the packet, i.e., the crystallite, grows from three, in the initial B-750 charcoal, to six, in the B-3000 charcoal. The reduction in the interplanar distance of the crystallites leads to an increase in x-ray density from 1.98 to 2.24  $\text{gm/cm}^3$ .

3. To determine the characteristic adsorbtional properties of the samples, and gain some idea of the elements making up their porous structure, the adsorption isotherms of benzene, cyclohexane, and water vapor were taken at  $20^\circ$ , over a wide range of equilibrium relative pressures, using the vacuum adsorbed weight method. The preliminary evacuation of the samples was carried out at  $450^\circ$  to a residual pressure  $\sim 1 \cdot 10^{-6}$  mm Hg.

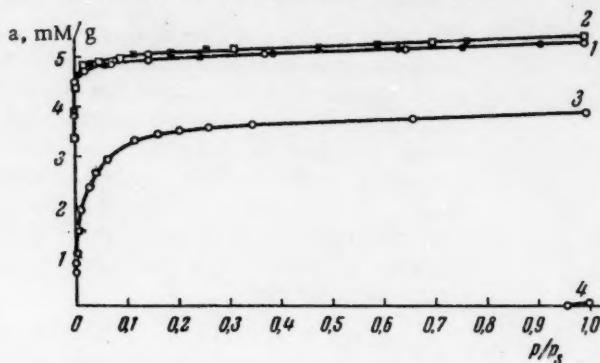


Fig. 2. Adsorption isotherms of benzene vapor at  $20^\circ$  for the charcoals. 1) B-750; 2) B-1300; 3) B-1750; 4) B-2300.

Figures 2 and 3 show the adsorption isotherms of benzene and cyclohexane vapor on the charcoal samples over the medium and high range of relative pressures. In the adsorption of benzene vapor on B-750 and B-1300 charcoal (Fig. 2), the time required to establish a state of adsorbtional equilibrium increases considerably on going to high relative pressures. The adsorption and desorption points lie on practically one and the same curve, and hysteresis loops are absent (curves 1 and 2). Heat treating the initial B-750 charcoal at  $1300^\circ$  does not produce any substantial change in either the porous structure of the charcoal, or the way it adsorbs benzene. There is even a clearly defined tendency toward a small increase in adsorption with B-1300 charcoal. The adsorption isotherms of B-750 and B-1300 charcoal rise very sharply in the small pressure region, and at relative pressures of about 0.1, the filling of the adsorbtional volume is practically complete.

The 1750° heat treatment of the B-750 charcoal produces a substantial lowering of the adsorbitivity of the 1750° sample (curve 3, Fig. 2). The isotherm rises much more gradually in the low relative pressure region. However, the most characteristic change in the charcoal structure appears in the form of a considerable reduction in the adsorption rate. In spite of long adsorption times allowed for each point on the isotherm (more than 24 hr for the medium and high relative pressure range), a state of true adsorbent equilibrium is never quite reached. As a result, curve 3 of Fig. 2 is not an equilibrium adsorption isotherm.

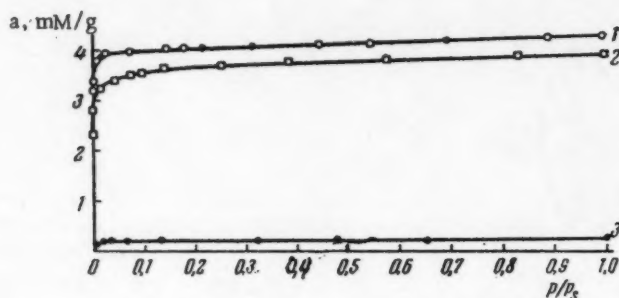


Fig. 3. Adsorption isotherms of cyclohexane vapor at 20° for the charcoals. 1) B-750; 2) B-1300; 3) B-1750.

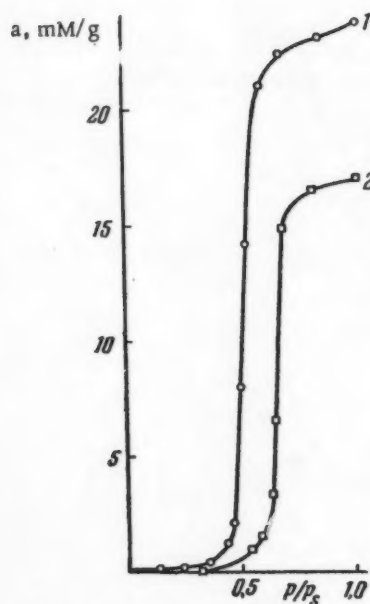


Fig. 4. Sorption isotherms of water vapor at 20° for the charcoals. 1) B-750; 2) B-1750.

The desorption rate is reduced to an even greater degree, especially for low relative pressures. Thus, the ratio of the adsorption values, corresponding to the desorption and adsorption branches of the nonequilibrium adsorption isotherms, comes to 1.10 for  $p/p_s = 0.1$ , 1.85 for  $p/p_s = 0.01$ , and 4.26 for  $p/p_s = 0.001$ . It is probable that the desorption branch is further removed from the equilibrium isotherm than the experimentally determined nonequilibrium adsorption branch (curve 3, Fig. 2).

If we go to a molecule of more complicated configuration, like cyclohexane, we observe an even more substantial decrease in the adsorption rate, which appears clearly on B-1750 charcoal. As a result, even the desorption branch of the B-1750 isotherm is located exceedingly low (Fig. 3, curve 3), and this sample of charcoal differs ten-fold in the experimentally realizable adsorbitivity for benzene and cyclohexane vapor. Unlike the adsorption isotherm of benzene, the cyclohexane isotherm for B-1300 charcoal is located somewhat lower than for the initial B-750 charcoal. In the present case, this is due in larger measure to change in structure of the charcoal than to purely kinetic effects.

Figure 4 shows the sorption branches of the adsorption isotherms of water vapor for typical samples of the B-750 and B-1750 charcoals of the series under investigation. The curves are similar in form, and the heat treatment of the initial charcoal shows up as a displacement of the region of sharp rise in the B-1750 isotherm toward the high relative pressure side. The reduction in the limiting sorbed volume of water vapor on going from B-750 charcoal to B-1750 is practically the same as the reduction observed with benzene vapor.

Table 2 gives the basic information on the structural parameters of the series B activated charcoal samples. The adsorption values,  $a_{mi}$ , corresponding to complete filling of the micropore volumes, were found from the benzene adsorption isotherms at the relative pressure  $p/p_s = 0.175$  [3]. In the case of cyclohexane, the  $a_{mi}$  values corresponded to  $p/p_s = 0.158$ , i.e., on the theory of capillary condensation, the relative pressure for the condition of equality of radii of the pores, calculated by Kelvin's equation. The quantity  $a$  represents the limiting sorption value at  $p/p_s = 1$ . In calculating the volumes of the micropores,  $v_{mi}$  and the limiting sorbed volumes,  $v_s$ , the

values taken for the volume of a millimole of material were  $v = 0.0888 \text{ cm}^3/\text{mM}$  for benzene,  $v = 0.108 \text{ cm}^3/\text{mM}$  for cyclohexane, and  $0.018 \text{ cm}^3/\text{mM}$  for water, corresponding to the density of the liquid phase in volume. The volumes of the medium-sized pores,  $v_p$ , were taken to be the differences between the limiting sorbed volumes,  $v_s$ , and the micropore volumes  $v_{mi}$ .

TABLE 2. Structural Parameters of Series B Charcoal Samples

| Charcoal | Vapor                     | $a_{mi}$<br>mM/g | $a_s$<br>mM/g | $v_{mi}$<br>$\text{cm}^3/\text{g}$ | $v_p$<br>$\text{cm}^3/\text{g}$ | $v_s$<br>$\text{cm}^3/\text{g}$ |
|----------|---------------------------|------------------|---------------|------------------------------------|---------------------------------|---------------------------------|
| B-750    | $\text{C}_6\text{H}_6$    | 4,97             | 5,21          | 0,442                              | 0,022                           | 0,464                           |
|          | $\text{C}_6\text{H}_{12}$ | 4,05             | 4,21          | 0,438                              | 0,017                           | 0,455                           |
|          | $\text{H}_2\text{O}$      | —                | 23,6          | —                                  | —                               | 0,425                           |
| B-1300   | $\text{C}_6\text{H}_6$    | 5,04             | 5,30          | 0,448                              | 0,023                           | 0,471                           |
|          | $\text{C}_6\text{H}_{12}$ | 3,63             | 3,85          | 0,392                              | 0,024                           | 0,416                           |
| B-1750   | $\text{C}_6\text{H}_6$    | —                | 3,79          | —                                  | —                               | 0,337                           |
|          | $\text{C}_6\text{H}_{12}$ | —                | 0,283         | —                                  | —                               | 0,031                           |
|          | $\text{H}_2\text{O}$      | —                | 17,0          | —                                  | —                               | 0,306                           |
| B-2300   | $\text{C}_6\text{H}_6$    | —                | 0,031         | —                                  | —                               | 0,003                           |
| B-3000   | $\text{C}_6\text{H}_6$    | —                | 0,060         | —                                  | —                               | 0,005                           |

TABLE 3. Constants in the Adsorption Isotherm Equation

| Vapor                     | Char-coal | $a_0$<br>mM/g | $W_0$<br>$\text{cm}^3/\text{g}$ | $B \cdot 10^4$ | $\beta$ | Range of applicability<br>$p/p_s$     |
|---------------------------|-----------|---------------|---------------------------------|----------------|---------|---------------------------------------|
| $\text{C}_6\text{H}_6$    | B-750     | 5,94          | 0,527                           | 0,482          | 1,00    | $3 \cdot 10^{-6} - 6 \cdot 10^{-3}$   |
|                           | B-1300    | 5,75          | 0,510                           | 0,597          | 1,00    | $3 \cdot 10^{-6} - 1,3 \cdot 10^{-2}$ |
|                           | B-1750    | 3,31          | 0,294                           | 2,23           | 1,00    | $4 \cdot 10^{-5} - 6 \cdot 10^{-3}$   |
| $\text{C}_6\text{H}_{12}$ | B-750     | 4,79          | 0,517                           | 0,482          | 1,07    | $6 \cdot 10^{-6} - 6 \cdot 10^{-3}$   |
|                           | B-1300    | 4,65          | 0,503                           | 0,597          | 0,94    | $2 \cdot 10^{-5} - 2 \cdot 10^{-3}$   |

For the initial B-750 charcoal, the limiting sorbed volumes, found from experiments with different vapors, do not differ materially from one another. Likewise, the micropore volumes, calculated from the adsorption isotherms of benzene and cyclohexane vapor, are practically identical. In the case of B-1300 charcoal, there is a reduction of one and the same value,  $\Delta v = 0.055 \text{ cm}^3/\text{gm}$ , both in the limiting sorbed volume, and in the micropore volume, on going from benzene to cyclohexane, which has bigger molecules. The volumes of the medium-sized pores in the B-750 and B-1300 charcoals, calculated from the experiments with different vapors, do not differ at all materially from one another. With B-1750 charcoal, the adsorption isotherms for organic vapors do not come to equilibrium, and therefore any measurement of the volumes of different types of pores is lacking in physical meaning. As far as the limiting sorbed volumes are concerned, the only thing that can be said about this sample is that there is a very large disparity of about ten-fold between the adsorbed volume of benzene, and the adsorbed volume of cyclohexane. The adsorptivity of the B-2300 and B-3000 charcoals is vanishingly small.

The isotherm equation given by the potential theory of adsorption for adsorbents of the first structural type [4], was fitted to the experimental adsorption isotherms for benzene and cyclohexane vapor. This equation has the form

$$\alpha = \frac{W_0}{v} e^{-\frac{B}{\beta^2} (\lg p_s/p)^2} \quad (1)$$

in which  $W_0$  is the limiting value of the adsorbent space, representing the volume of the micropores,  $B$  is a constant which depends on the dimensions of the micropores, and has a definite meaning in the enhanced adsorption potential effect, and  $\beta$  is a fitting factor for the characteristic curve. As a typical example, Fig. 5 shows the experimental adsorption isotherms of benzene and cyclohexane vapor on B-1300 charcoal, in the linear form of Eq. 1, and Table 3 gives the constants of the equation. The values of the constants for the nonequilibrium adsorption isotherm of benzene vapor on B-1750 charcoal have some orientational significance.

From the data of Table 3, it can be seen that raising the heat treatment temperature of B-750 charcoal, as was found previously with charcoal made out of phenolaldehyde resin [1], lowers the limiting volumes of the adsorbent space  $W_0$ , at the same time that it raises the constant  $B$  in the adsorption isotherm equation. It should be noted that

over the temperature range from 750° to 1300° the reduction in  $W_0$  is not very substantial, and the actual values of  $W_0$ , found from the experiments on benzene and cyclohexane, are close to one another. The difference between the limiting adsorbed quantities of benzene and cyclohexane,  $a_0 = W_0/v$ , is due, in the present case, to the difference between the volumes occupied by a millimole of these substances in the liquid state.

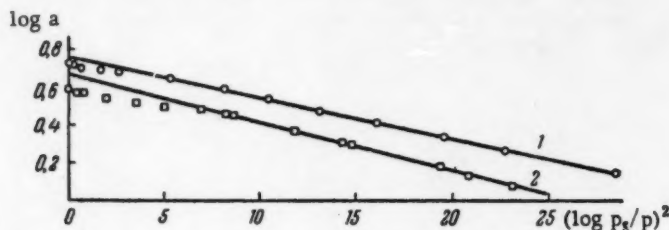


Fig. 5. Adsorption isotherms of benzene and cyclohexane vapor at 20° on B-1300 charcoal in the linear form of Eq. (1): 1) benzene; 2) cyclohexane.

One of the peculiarities of expressing the experimental data in the linear form of Eq. (1), for the case of finely-porous activated charcoals made from polyvinylidene chloride, which have small values of  $B$  in the adsorption isotherm equation ( $0.4 \cdot 10^{-6} - 0.5 \cdot 10^{-6}$ ), is the deviation of the experimental points from a straight line, in the high relative pressure region (Fig. 5). The experimental points fall below the straight lines, and therefore the limiting adsorbed quantities,  $a_0$ , exceed not only the values of  $a_{mi}$ , determined directly from the isotherms, but the limiting sorption values,  $a_s$ , as well. It should be noted further that the ratios of the values of  $a_0$ ,  $a_{mi}$ , and  $a_s$  for benzene and cyclohexane are practically identical for B-750 charcoal, and have the value  $1.233 \pm 0.006$ . For B-1300 charcoal, the ratio of the values of  $a_0$  is equal to 1.236, and the ratio of the values of  $a_{mi}$  and  $a_s$  is  $1.382 \pm 0.05$ .

#### DISCUSSION OF RESULTS

1. It is a matter of fundamental importance to analyze the reasons why the experimental points for charcoal made out of polyvinylidene chloride fall on the low adsorption side of the linear form of the adsorption isotherm equation (Fig. 5) in the medium and high relative pressure range. The departure from linearity is not substantial when nitrogen, which has smaller molecular dimensions, is adsorbed on a similar charcoal sample (Fig. 4 in [3]); it increases on going to benzene, and becomes considerable with cyclohexane, the adsorption of which proceeds at a substantially reduced rate (Fig. 5). The observed phenomenon is doubtless to a greater extent a matter of specific peculiarities of the microporous structure of activated charcoals made out of polyvinylidene chloride, than it is a matter of small micropore dimensions, as might be suspected from the low values of the constant  $B$ . Thus for charcoal made of V-3 sugar, activated in  $\text{CO}_2$  gas (Fig. 5 [6]), with  $W_0 = 0.202 \text{ cm}^3/\text{gm}$ , and a value of the constant as low as  $B = 0.433 \cdot 10^{-6}$  [4], the experimental points correspond well with the linear form of the isotherm equation (1) over the whole adsorbational range of equilibrium relative pressures from  $2 \cdot 10^{-5}$  to  $2 \cdot 10^{-1}$ .

The deviations from linearity at relative pressures above  $5 \cdot 10^{-3}$ , which are observed with B-750 and B-1300 charcoals, may be due both to peculiarities in the way the small micropores are filled up with adsorbed molecules, and to a slow-up in adsorption kinetics, i.e., it may not be possible to reach adsorbational equilibrium. These deviations start to appear at mean micropore saturation values  $a/a_{mi}$  equal to 0.89 for benzene, and 0.85 for cyclohexane. In the remaining volume of the adsorbational space, the molecules are possibly less densely packed, the larger their dimensions, and the more complicated their configuration. The ultraporosity effect may actually be playing its familiar role, i.e., the part of the adsorbational space belonging to the finer micropores is not accessible to the larger molecules to be adsorbed.

As a result, a reduction in the mean values of the density of the adsorbed substances is observed. The observed deviations may be explained by simply assuming a relative reduction in mean density of 12-16% for adsorbed benzene, and 15-19% for cyclohexane. Naturally, the kinetics of the process, if it plays any substantial role, will exert an additional effect in the same direction. Subsequently, some special experiments will be set up, dealing explicitly with the kinetics of the process, which will make it possible to select the most rational explanation of the observed deviations.

2. A more detailed x-ray structure analysis [7] of charcoal made from polyvinylidene chloride, subjected to 2 hr heat treatment at 1000° ( $s = 1300 \text{ m}^2/\text{gm}$  from the low temperature adsorption of nitrogen,  $a_m = 13.5 \text{ mm}^3/\text{gm}$ ,  $v_m = 0.47 \text{ cm}^3/\text{gm}$ ), which occupies an intermediate position between our samples B-750 and B-1300, established the fact that 65% of the carbon is in the form of highly perfect, plane, graphite-like grids with a diameter of  $16 \pm 1 \text{ \AA}$ , and 35% is in the unordered form. About 55% of the carbon grids are grouped in pairs of parallel layers, with an interplanar distance of  $3.7 \text{ \AA}$ , and about 45% of the grids remain mutually unoriented. These data are in general close to what we found, both for the interplanar distance  $(3.85 + 3.72)/2 = 3.79 \text{ \AA}$ , and for the diameter of the "crystallites" ( $L_a = 22 \text{ \AA}$  instead of  $16 \text{ \AA}$ ). The considerable amount of background on the microphotographs of samples B-750 and B-1300 (Fig. 1) shows that there is a substantial amount of unordered carbon present.

In contrast to the charcoals which are prepared by activation with gaseous agents, the microporous structure of the activated charcoal made from polyvinylidene chloride is not formed as a result of burning out individual crystallites. It is probable that the micropores of B-750 charcoal are, basically, fissure-like gaps between the crystallites or individual plane graphite grids. Judging from the smallness of the constant B in the adsorption isotherm equation, the distance between the opposite walls of the pores, i.e., the height of the fissure, is small, and comparable in size to the dimensions of the molecules being adsorbed. It is not highly probable that more than two or three layers of adsorbed molecules can be fitted into the fissure-like pores.

From the form of the isotherm for series B charcoals, the adsorption values  $a_{mi}$  corresponding with filling up the micropore volumes with two or three layers of adsorbed molecules, are, to a first approximation, close to the adsorption values of the B points on Brunauer's isotherms [8]. Therefore, the values of specific surface calculated from his curves cannot differ very materially from the correct ones. On the other hand, the bi-dispersion model of microporous structure [1] can be applied to B-750 and B-1300 charcoals. Reasonable parameters for this model are:  $n_1' = 1$ ,  $n_2' = 1$ ,  $n_1'' = 3$ , and  $n_2'' = 2$ , where the subscript 1 applies to benzene, and the subscript 2 applies to cyclohexane.

TABLE 4. Specific Surfaces of Charcoals in  $\text{m}^2/\text{gm}$

| Charcoal | X-ray surface |       |      | From sorption at $a_m = a_{mi}$ |             | from bi-dispersion model |          |
|----------|---------------|-------|------|---------------------------------|-------------|--------------------------|----------|
|          | $S_B$         | $S_T$ | $S$  | $C_6H_6$                        | $C_6H_{12}$ | $S$                      | $\alpha$ |
| B-750    | 920           | 1350  | 2270 | 1220                            | 870         | 980                      | 0,246    |
| B-1300   | 810           | 1300  | 2110 | 1250                            | 830         | 840                      | 0,02     |
| B-1750   | 730           | 1030  | 1760 | 940                             | <45-90*     |                          |          |
| B-2300   | 480           | 910   | 1390 | <8                              |             |                          |          |
| B-3000   | 360           | 500   | 860  | <8                              |             |                          |          |

\* The first figure corresponds to two adsorbed layers in the fissure-like pore, the second figure to one.

Table 4 gives the values of x-ray specific surfaces calculated by the method given in [1], and the specific surfaces found from sorption measurements, which can serve as a preliminary orientational analysis. The molecular area  $41 \text{ \AA}^2$  was used for benzene, and  $38 \text{ \AA}^2$  for cyclohexane.

The x-ray surface values give only orientational, upper potential values for the specific surfaces of the charcoals, under the assumption that they consist only of assemblies of crystallites. The assumption  $a_m = a_{mi}$  leads to a substantial difference between the specific surfaces determined from experiments on benzene, and those found with cyclohexane. This could, in principle, be due to the ultraporosity effect, which is especially pronounced in the B-1750 charcoal. But it is better to recognize that these values of specific surface have only semiquantitative significance. The bi-dispersion model leads to reasonable values for the specific surfaces, but the parameters involved require independent substantiation. The concepts which we have presented are only orientational, and they will be refined in the subsequent development of the investigation, through the use of a number of additional techniques.

3. Heat treating the initial B-750 charcoal at 1750° for 45 min produces the charcoal sample B-1750, which shows an exceedingly pronounced difference in adsorptivity between benzene and cyclohexane vapor, suggesting a

molecular screening action [9]. However, the peculiar thing about this case is the fact that the selective adsorption shows up with benzene and cyclohexane molecules, which are not of particularly different dimensions, and, moreover, belong to the same group of substances in the molecular screen classification [9]. Table 5 gives a comparison of the results of our experiments with synthetic zeolite — a commercial sample of Linde 5A molecular screen (MS — 5A), and B-1750 charcoal. The adsorption values were interpolated between various values of relative pressure on

TABLE 5. Interpolated Values of Adsorption for Different Relative Pressures

| Sorbent | Vapor                              | a, mm/g at the relative pressures |                      |                      |                      |      |
|---------|------------------------------------|-----------------------------------|----------------------|----------------------|----------------------|------|
|         |                                    | 1 · 10 <sup>-4</sup>              | 1 · 10 <sup>-3</sup> | 1 · 10 <sup>-2</sup> | 1 · 10 <sup>-1</sup> | 1    |
| MS-5A   | H <sub>2</sub> O 20°               | —                                 | 4,92                 | 8,70                 | 10,30                | 15,3 |
|         | N <sub>2</sub> —195°               | 4,68                              | 5,35                 | 5,87                 | 6,22                 | 7,95 |
|         | C <sub>6</sub> H <sub>6</sub> 20°  | 0                                 | 0                    | 0                    | 0,017                | 2,38 |
|         | C <sub>6</sub> H <sub>12</sub> 20° | 0                                 | 0                    | 0,014                | 0,024                | 1,62 |
| B-1750  | C <sub>6</sub> H <sub>6</sub> 20°  | 1,49                              | 2,51                 | 3,19                 | 3,40                 | 3,79 |
|         | C <sub>6</sub> H <sub>12</sub> 20° | 0,05                              | 0,11                 | 0,17                 | 0,21                 | 0,28 |

the adsorption isotherms. The nitrogen and water molecules penetrate through the "windows" in the elementary cavities, and are thus substances which are adsorbable by the MS — 5A, while the "windows" remain impenetrable to benzene and cyclohexane molecules. Any adsorption of the latter is due simply to secondary porous structure [10]. The interpolated adsorption values for B-1750 charcoal are from the desorption branch of the isotherm.

According to the data of Table 5, there is no qualitative difference between the adsorptivity of the MS — 5A molecular screen for nitrogen or water vapor, on the one hand, and benzene or cyclohexane, on the other, and that of the B-1750 charcoal, for benzene, on the one hand, and cyclohexane on the other. The molecular screening action

of the B-1750 charcoal is due, both to the peculiarities of its microporous structure, which may also be characterized by more or less narrow entrances or "windows" leading to pores having more or less wide fissure-like cavities, and to the differences in the kinetics of adsorption, which are bound up with the porous structure. Subsequently, on the basis of more detailed investigation, we intend to evaluate the roles actually played by microporous structure and adsorption kinetics in the molecular screening effect which we have been observing.

In conclusion, the authors consider that they have a pleasant debt of gratitude to be expressed to S. G. Tolkahev and I. V. Uspenskiy for carrying out the high temperature heat treatment of the charcoal.

#### SUMMARY

1. X-ray structure and adsorption studies have been made on a series of charcoal samples prepared by heat treating charcoal made from polyvinylidene chloride. The heat treatment temperatures extended up to 3000°.

2. An analysis is made of the peculiarities of the change produced in the microporous structure and adsorptivity of the charcoals. It is shown it is possible, in principle, to prepare carbonaceous adsorbents which exhibit a pronounced molecular screening action.

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KINETICS OF DEHYDROGENATION AND DEHYDRATION  
OF ISOPROPYL ALCOHOL ON TITANIUM DIOXIDE  
(ANATASE)

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In connection with the rapid growth in production of titanium dioxide, it is somewhat to the point to investigate its catalytic properties. However, up to the present time,  $\text{TiO}_2$  has been numbered among the catalysts that have received little study. Bischoff and Adkins [1, 2] studied the reactions of alcohols, simple and compound ethers, and formic and acetic acids on various samples of titanium dioxide. The transformations of ethyl alcohol on two modifications of  $\text{TiO}_2$ , anatase and rutile, were studied by Rubinshtein and Kulikov [3, 4]. It was shown that anatase is the more active catalyst, and promotes dehydration of the alcohol, while rutile is basically a dehydrogenator of the alcohol. The same conclusion is reached by Schwab [5]. The reactions of ethyl alcohol on titanium dioxide were also studied by Engelder [6]. Titanium dioxide produces isomerization and irreversible catalysis in cyclohexene [7], and is used for the hydration of mineral oil [8], for the oxidation of n-butene, benzene, butane, butyl and isopropyl alcohol, and a number of unsaturated compounds [9], as well as for hydrocarbon conversion [10].  $\text{TiO}_2$  turns out to be one of the best catalysts for the esterification of acetic acid with various alcohols [11, 12], it gives a high yield in the dehydration of orthoethylaniline to indole [13], induces the dehydrocyclization of n-hexane [14], deuterium exchange [15], and the ortho-para hydrogen transformation [16]. Titanium dioxide is a semiconductor, and adding small quantities to other semiconductors, such as iron oxide, considerably changes the catalytic properties of the latter in the dehydrogenation and dehydrocyclization of hydrocarbons [17].

We have shown previously [18], that  $\text{TiO}_2$  dehydrogenates and dehydrates ethyl, n-propyl, and isopropyl alcohol, and likewise induces dehydrogenation and irreversible catalysis of cyclohexene and cyclohexadiene, and dehydrogenation of cyclohexane. The transformation of the above substances on  $\text{TiO}_2$  is accompanied by carbonation of the  $\text{TiO}_2$ , which changes the activity and selectivity of the catalyst during the course of the experiment. Thus, in the first minutes after the start of the experiment, the isopropyl alcohol is undergoing dehydrogenation practically exclusively on  $\text{TiO}_2$ , but 15-20 min later, nothing but dehydration is taking place. With ethyl or n-propyl alcohol, an increase in the dehydration rate also takes place, although the dehydrogenation reaction is not completely suppressed. The gradual carbonation of the anatase surface, which occurs in the course of the experiment inhibits the irreversible catalysis of cyclohexene and cyclohexadiene, while accelerating the dehydrogenation of cyclohexene, cyclohexadiene and cyclohexane.

The present paper is a study of the kinetics of the dehydrogenation and dehydration of isopropyl alcohol on  $\text{TiO}_2$  (anatase).

#### EXPERIMENTAL

The preparation of the catalyst, the apparatus, and the technique of carrying out the experiments have been described in an earlier paper [18]. The hydrogen and nitrogen used in the work were purified of oxygen by passing them at  $190^\circ$  through a column (height 760 mm, internal diameter 30 mm) filled with activated copper on kieselguhr [19], and were dried over solid caustic alkali and silica-gel. The propylene was prepared by dehydrating isopropyl alcohol over aluminum oxide at  $350-370^\circ$ . Chromatographic analysis showed that the propylene was free of contaminants. The constants of the alcohol and the acetone agreed with known values from the literature. Gas was admitted at the desired rate from an automatic gasometer by a universal impulse reducing valve [20]. All the gas volumes were reduced to normal temperature and pressure. The kinetic studies were made on one and the same sample of catalyst, prepared by hydrolysis of titanium tetrachloride with distilled water (catalyst I). The volume

of the sample of catalyst was 6.4 ml, the weight was 5.1 gm, and the length of the layer was 20 mm. All the kinetic studies were made at the same degree of carbonation of the catalyst, which was determined from the EMF of a differential thermocouple [18] as given on the curve of EMF against time from the beginning of the experiment.

To study the kinetics of incompletely carbonated  $\text{TiO}_2$ , the kinetic measurements were made starting from the moment at which the EMF of the thermocouple stopped changing. The reproducibility of the experiments was always checked after regenerating the catalyst.

Calculation of the  $K_p$  values, and the degree of equilibrium of the reaction showed that all the kinetic experiments were made under conditions far removed from equilibrium.

For the kinetic study of monomolecular heterogeneous catalysis reactions, the theory [21] gives a general equation, which, when applied to the dehydrogenation or dehydration of a monatomic alcohol (e.g., isopropyl) may be written as follows:

$$k = A_1 (Z_2 - Z_3) \ln \frac{A_1}{A_1 - m} - (Z_2 + Z_3 - 1) m \quad (1)$$

Here,  $A_1$  is the volume of propylene or hydrogen formed per minute, with 100% transformation of the alcohol, introduced at a given rate  $\underline{v}$ , for dehydration and dehydrogenation, respectively;  $\underline{m}$  is the volume of propylene or hydrogen formed per minute when the isopropyl alcohol is introduced at the rate  $\underline{v}$ ; and  $Z_2$  and  $Z_3$  are the relative adsorption coefficients of the reaction products (hydrogen and acetone in the case of dehydrogenation, propylene and water in the case of dehydration) equal to the ratio of the absolute adsorption coefficients of the reaction products to the initial alcohol. The values of  $Z_2$  and  $Z_3$  were calculated from Eq. (2), which follows from the same general kinetic equation [21], for small degrees of transformation [22].

$$Z = \left( \frac{m_0}{m} - 1 \right) / \left( \frac{100}{p} - 1 \right) \quad (2)$$

where  $m_0$  and  $\underline{m}$  are the quantity of reaction product formed (in the vapor state at standard conditions) for the conditions, respectively, of introducing the pure alcohol, and its having reached  $P$  mole percent of the mixture with the reaction product, for which the relative adsorption coefficient  $Z$  is being determined. Here it is important for the total number of moles entering into the experiments with either the pure alcohol or its binary mixtures with the reaction products to remain constant, whether the reaction is dehydrogenation or dehydration.

Since  $Z$  is the equilibrium constant for the adsorptional replacement of isopropyl alcohol by acetone, hydrogen, propylene, or water from the catalytically active centers of the surface, it is easy to calculate the free energy change  $\Delta F$ , the entropy change  $\Delta S$ , and the change in heat content  $\Delta H$  [23, 24] for the reaction from the usual thermodynamic formulas, thus:

$$\begin{aligned} \Delta F &= -RT \ln Z \quad (a); \quad \Delta H = \frac{4.575 \cdot T_1 \cdot T_2 (\lg Z_1 - \lg Z_2)}{T_2 - T_1} \quad (b) \\ \Delta S &= \frac{\Delta H - \Delta F}{T} \quad (c) \end{aligned} \quad (3)$$

Thus, finding the kinetic equations for the monomolecular reaction in question is a matter of finding the values of  $Z$  for all the reaction products at different temperatures. Substituting the values of  $Z_2 + Z_3$ ,  $A$ , and  $\underline{m}$  in Eq. (1), we find the values of the rate constants at different temperatures. From the temperature dependance of  $k$  it is easy to find the activation energy, and the value of the exponential coefficient  $k_0$ . Knowing  $\epsilon$ ,  $k_0$  and the temperature dependance of  $Z_2$  and  $Z_3$ , as given by Eq. (3b), it is always possible to calculate what  $\underline{m}$ , the activity of the catalyst, will be for any given conditions under which the experiment is conducted (temperature, admission rate  $\underline{v}$ , etc.).

Tables 1-2 give the data for calculating the relative adsorption coefficients of acetone on practically uncarbonated and partially carbonated  $\text{TiO}_2$ . Since the carbon deposition goes on from the very start of the reaction, it is more correct to consider the data of these tables as having to do with varying degrees of carbonation of the  $\text{TiO}_2$ . As follows from Tables 1-2 (Fig. 1), the relative adsorption coefficient of acetone changes very little with changes in the degree of carbonation of the  $\text{TiO}_2$ , but it changes considerably with changes in temperature range 276-306°; the relative adsorption coefficient of hydrogen does not change on the partially carbonated  $\text{TiO}_2$  (Table 3).

TABLE 1. Relative Adsorption Coefficients (Z) of Acetone on Uncarbonated TiO<sub>2</sub>

| Temperature °C | Alcohol content in mixture mole % | mH <sub>2</sub> ml/min (experimental) | mH <sub>2</sub> ml/min calculated from Z for acetone, comp. | Z of acetone |
|----------------|-----------------------------------|---------------------------------------|---|--------------|
| 282            | 100                               | 24,5                                  | 24,7  |              |
|                | 100                               | 25,0                                  |   |              |
|                | 85                                | 17,9                                  |   |              |
|                | 75                                | 15,2                                  |   |              |
|                | 65                                | 11,9                                  |   |              |
|                | 55                                | 8,8                                   |   |              |
|                | 55                                | 7,5                                   |   |              |
|                | 45                                | 5,6                                   |   |              |
|                | 45                                | 5,7                                   |   |              |
| Mean           |                                   |                                       | 2,4   |              |
| 294            | 100                               | 29,1                                  | 30,3  |              |
|                | 100                               | 31,6                                  |   |              |
|                | 75                                | 18,5                                  |   |              |
|                | 75                                | 19,4                                  |   |              |
|                | 65                                | 16,4                                  |   |              |
|                | 55                                | 12,5                                  |   |              |
|                | 45                                | 9,3                                   |   |              |
|                | Mean                              |                                       |   |              |
| 310            | 100                               | 39,8                                  | 39,5  |              |
|                | 100                               | 39,2                                  |   |              |
|                | 85                                | 33,7                                  |   |              |
|                | 85                                | 34,0                                  |   |              |
|                | 65                                | 24,0                                  |   |              |
|                | 55                                | 18,1                                  |   |              |
|                | 45                                | 13,4                                  |   |              |
|                | Mean                              |                                       |   |              |

TABLE 2. Relative Adsorption Coefficients of Acetone on Partially Carbonated TiO<sub>2</sub>

| Temperature °C | Alcohol content in mixture mole % | Gas analysis, % |        | m, ml/min of gas (experimental) | mH <sub>2</sub> ml/min | mH <sub>2</sub> ml/min calculated from Z for acetone, comp. | Z of acetone |
|----------------|-----------------------------------|-----------------|--------|---------------------------------|------------------------|---|--------------|
|                |                                   | H <sub>2</sub>  | unsat. |                                 |                        |   |              |
| 282            | 100                               | 87,4            | 12,6   | 25,0                            | 21,8                   | 14,7  | 2,9          |
|                | 85                                | 80,9            | 19,1   | 17,9                            | 14,5                   |   |              |
|                | 75                                | 82,7            | 17,3   | 15,2                            | 12,6                   |   |              |
|                | 65                                | 80,5            | 19,5   | 11,9                            | 9,6                    |   |              |
|                | 55                                | 79,0            | 21,0   | 7,5                             | 6,5                    |   |              |
|                | 45                                | 80,5            | 19,5   | 5,6                             | 4,5                    |   |              |
|                | Mean                              |                 |        |                                 |                        | 2,7   |              |
| 294            | 100                               | 90,8            | 9,2    | 31,6                            | 28,7                   | 25,6  | 1,6          |
|                | 85                                | 89,4            | 10,6   | 25,3                            | 22,6                   |   |              |
|                | 65                                | 84,0            | 16,0   | 16,4                            | 13,8                   |   |              |
|                | 55                                | 88,3            | 11,7   | 12,5                            | 11,0                   |   |              |
|                | 45                                | 100,0           | 0,0    | 9,3                             | 9,3                    |   |              |
|                | Mean                              |                 |        |                                 |                        | 1,8   |              |
| 310            | 100                               | 78,3            | 20,5   | 39,8                            | 31,4                   | 25,7  | 0,9          |
|                | 75                                | 90,0            | 10,0   | 27,0                            | 24,3                   |   |              |
|                | 65                                | 95,7            | 4,3    | 24,0                            | 23,0                   |   |              |
|                | 55                                | 94,2            | 5,8    | 18,1                            | 17,0                   |   |              |
|                | 45                                | 100,0           | 0,0    | 13,4                            | 13,4                   |   |              |
|                | Mean                              |                 |        |                                 |                        | 0,9   |              |

Tables 4-7 give the data for calculating the relative adsorption coefficients of water (Table 4), and propylene (Table 5) on the partially carbonated surface of the TiO<sub>2</sub>. The adsorption coefficient of water falls from 1.9 to 0.9 on raising the temperature from 280 to 310°. The adsorption coefficient of propylene does not change in the range 300-330°. The values of ΔH were calculated from the temperature dependence of the relative adsorption coefficients of acetone and water. In addition, values were calculated for ΔS and ΔF (Tables 6 and 7).

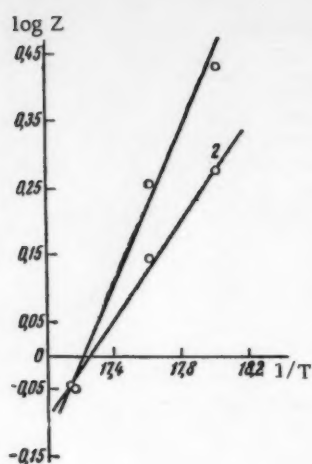


Fig. 1. 1) For adsorbtional replacement of alcohol by acetone (1); 2) for the adsorbtional replacement of alcohol by water (2).

TABLE 3. Relative Adsorbtion Coefficients of Hydrogen on Partially Carbonated  $\text{TiO}_2$  Catalyst

| Temp. °C | Alcohol content in mixture mole % | $m_{\text{H}_2}$ ml/min (experimental) | $m_{\text{H}_2}$ ml/min calculated from $Z_{\text{H}_2}$ | $Z_{\text{H}_2}$ |
|----------|-----------------------------------|--|--|------------------|
| 272      | 100                               | 6,4                                    |  |                  |
|          | 87,5                              | 5,5                                    |  | 5,6              |
|          | 76,9                              | 5,4                                    |  | 5,0              |
|          | 73,2                              | 4,7                                    |  | 4,8              |
|          |                                   |  | Mean   | 0,9              |
| 295      | 100                               | 20,7                                   | 21,1   |                  |
|          | 100                               | 21,6                                   |  |                  |
|          | 88                                | 18,2                                   |  | 18,7             |
|          | 71,2                              | 15,6                                   |  | 15,5             |
|          | 66                                | 14,9                                   |  | 14,5             |
|          |                                   |  | Mean   | 0,9              |
| 306      | 100                               | 38,0                                   |  |                  |
|          | 83,6                              | 32,0                                   |  | 32,2             |
|          | 77,9                              | 33,3                                   |  | 30,4             |
|          |                                   |  | Mean   | 0,9              |

TABLE 4. Relative Adsorbtion Coefficient of Water on Partially Carbonated  $\text{TiO}_2$  Catalyst

| Temperature °C | Alcohol content in mixture, mole % | Gas analysis % |              | $m$ , ml/min of gas (experimental) | $m$ , ml/min (unsat.) | $m$ , ml/min (unsat.) calculated from $Z_{\text{H}_2\text{O}}$ | $Z_{\text{H}_2\text{O}}$ |
|----------------|------------------------------------|----------------|--------------|------------------------------------|-----------------------|--|--------------------------|
|                |                                    | $\text{H}_2$   | undetermined |                                    |                       |  |                          |
| 282            | 100                                | 68,0           | 32,0         | 27,8                               | 8,6                   |  | 2,1                      |
|                | 75                                 | 71,0           | 28,4         | 17,8                               | 5,1                   |  | 1,8                      |
|                | 75                                 | 69,2           | 29,0         | 18,7                               | 5,4                   | 5,3  |                          |
|                | 65                                 | 72,6           | 26,2         | 17,5                               | 4,6                   |  | 1,6                      |
|                | 55                                 | 76,2           | 21,8         | 16,7                               | 3,6                   | 3,4  | 1,7                      |
|                | 45,8                               | 81,0           | 17,8         | 15,2                               | 2,7                   | 2,7  | 1,8                      |
|                |                                    |                |              |                                    |                       | Mean   | 1,9                      |
| 294            | 100                                | 62,4           | 37,6         | 33,0                               | 12,5                  |  |                          |
|                | 65                                 | 69,2           | 30,1         | 24,5                               | 7,4                   | 7,2  | 1,3                      |
|                | 55                                 | 73,5           | 26,5         | 20,3                               | 5,4                   | 5,8  | 1,6                      |
|                | 45,8                               | 73,6           | 26,3         | 18,7                               | 4,9                   | 4,7  | 1,4                      |
|                |                                    |                |              |                                    |                       | Mean   | 1,4                      |
| 310            | 100                                | 66,1           | 33,8         | 44,5                               | 14,8                  |  |                          |
|                | 85                                 | 65,5           | 33,4         | 38,9                               | 13,0                  |  |                          |
|                | 85                                 | 67,0           | 32,6         | 40,8                               | 13,3                  | 12,7   | 0,8                      |
|                | 75                                 | 68,6           | 31,2         | 37,1                               | 11,6                  | 11,4   |                          |
|                | 75                                 | 68,0           | 31,0         | 37,1                               | 11,6                  | 11,4   | 0,9                      |
|                | 65                                 | 70,0           | 29,8         | 34,1                               | 10,2                  | 10,0   | 0,9                      |
|                | 55                                 | 75,2           | 24,2         | 28,6                               | 6,9                   | 8,4  | 1,4                      |
|                | 45,8                               | 70,5           | 28,6         | 23,6                               | 6,7                   | 7,1  | 1,0                      |
|                |                                    |                |              |                                    |                       | Mean   | 0,9                      |

From the data obtained from Eq. (1), calculations were made of the actual rate constants for the dehydration of isopropyl alcohol on partially carbonated  $\text{TiO}_2$  (Table 8), as well as the values of the actual activation energy of

TABLE 5. Relative Adsorption Coefficients of Propylene on Partially Carbonated  $\text{TiO}_2$  Catalyst (mixtures of isopropyl alcohol and propylene)

| Temp., °C | Alcohol content in mixture mole % | m, ml/min propylene on passing pure alcohol (experimental) | m, ml/min propylene on passing mixture | m, ml/min propylene calculated from $Z_{\text{propylene comp.}}$ | $Z_{\text{propylene}}$ |
|-----------|-----------------------------------|--|--|--|------------------------|
| 300       | 100                               | 27,0   |  |  |                        |
|           | 71,0                              | 24,8   | 22,9                                   | 22,9   | 0,3                    |
|           | 58,5                              | 22,5   | 19,9                                   | 19,9   | 0,2                    |
|           | 50,2                              | 22,8   | 17,8                                   | 17,8   | 0,2                    |
|           |                                   |  |  | Mean   | 0,2                    |
| 330       | 100                               | 38,7   |  |  |                        |
|           | 83,7                              | 35,2   | 34,4                                   | 34,4   | 0,2                    |
|           | 71,0                              | 32,1   | 30,4                                   | 30,4   | 0,2                    |
|           | 58,5                              | 30,0   | 25,6                                   | 25,6   | 0,2                    |
|           | 50,2                              | 26,8   | 22,8                                   | 22,8   | 0,2                    |
|           |                                   |  |  | Mean   | 0,2                    |

TABLE 6. Values of  $\Delta H$ ,  $\Delta S$ , and  $\Delta F$  for the Adsorptional Replacement of Isopropyl Alcohol by Acetone on Partially Carbonated  $\text{TiO}_2$

| Temperature, °C | $Z_{\text{acetone}}$ | $\Delta F$ , cal/mole | $\Delta S$ , cal/deg. mole | $\Delta H$ , cal/mole |
|-----------------|----------------------|-----------------------|----------------------------|-----------------------|
| 282             | 2,7                  | -1090,0               | 43,8                       | 23 100                |
| 294             | 1,8                  | -665,0                | 41,9                       |                       |
| 310             | 0,9                  | +122,0                | 39,4                       |                       |

TABLE 7. Values of  $\Delta H$ ,  $\Delta S$ , and  $\Delta F$  for the Adsorptional Replacement of Isopropyl Alcohol by Water on Partially Carbonated  $\text{TiO}_2$

| Temp., °C | $Z_{\text{H}_2\text{O}}$ | $\Delta F$ , cal/M | $\Delta S$ , cal/deg. mole | $\Delta H$ , cal/mole |
|-----------|--------------------------|--------------------|----------------------------|-----------------------|
| 282       | 1,9                      | -707,0             | 31,8                       | 16 900                |
| 294       | 1,4                      | -378,0             | 30,4                       |                       |
| 310       | 0,9                      | 122,0              | 28,2                       |                       |

TABLE 8. True Activation Energy of the Dehydration of Isopropyl Alcohol on Partially Carbonated  $\text{TiO}_2$  (Rate of introduction of alcohol 0,224 ml/min,  $\epsilon_{\text{H}_2\text{O}} = 26,400$  cal/mole;  $k_0 \text{ comp.} = 3,1 \cdot 10^{10}$ )

| Temperature °C | $Z_{\text{H}_2\text{O}}$ | $Z_{\text{propylene}}$ | $k$ , ml/min | $k$ , ml/min · ml · cat | $\log k_0$ | $\frac{\epsilon}{\log k_0} \cdot 10^{-3}$ |
|----------------|--------------------------|------------------------|--------------|-------------------------|------------|---|
| 266            | 3,1                      | 0,0                    | 3,9          | 0,61                    | 10,50      | 2,51                                      |
| 282            | 1,9                      | 0,0                    | 10,3         | 1,54                    | 10,59      | 2,49                                      |
| 294            | 1,4                      | 0,2                    | 14,5         | 2,27                    | 10,54      | 2,50                                      |
| 310            | 0,9                      | 0,2                    | 18,6         | 2,66                    | 10,32      | 2,56                                      |
| Mean           |                          |                        |              |                         |            | 2,52                                      |

the dehydration, the exponential coefficient  $k_0$ , and the ratio  $\epsilon \cdot 10^{-3} / \log k_0$ . The actual value of  $\epsilon_{\text{H}_2\text{O}}$  turned out to be 2 kilo-cal/mole greater than the apparent  $\epsilon_{\text{H}_2\text{O}}$ .

A similar calculation of the actual activation energy  $\epsilon_{H_2}$  for the dehydrogenation of the alcohol on uncarbonated  $TiO_2$  (Table 9) gave a value of  $\epsilon_{H_2}$  equal to 15.4 kilo-cal/mole (as against 11.9 for the apparent activation energy).

TABLE 9. True Activation Energy of the Dehydrogenation of Isopropyl Alcohol on Uncarbonated  $TiO_2$  ( $\epsilon_{H_2} = 15.4$  kilo-cal/mole,  $V_{cat} = 6.4$  ml,  $k_0 = 7.8 \cdot 10^6$ ; rate of introduction 0.0294 ml/min)

| Temperature °C | m    | $Z_{H_2}$ | Z acetone | $k$ ,<br>ml/min · ml | $k$ ,<br>ml/min · ml · cat | log $k_0$ | $\frac{\epsilon}{\log k_0} \cdot 10^{-3}$ |
|----------------|------|-----------|-----------|----------------------|----------------------------|-----------|---|
|                |      |           |           |                      |                            |           |   |
| 282            | 24,7 | 0,9       | 2,7       | 43,3                 | 6,78                       | 6,91      | 2,23                                      |
| 294            | 30,3 |           | 1,8       | 56,8                 | 8,88                       | 6,88      | 2,24                                      |
| 310            | 39,5 |           | 1,2       | 82,5                 | 1,29                       | 6,88      | 2,24                                      |
| Mean           |      |           |           |                      |                            | 6,89      | 2,24                                      |

#### SUMMARY

1. This is the first study that has been made of the detailed kinetics of the dehydrogenation and dehydration of isopropyl alcohol on  $TiO_2$ , complicated by carbonation of the catalyst.
2. The carbonation of the  $TiO_2$  has little effect on the values of the relative adsorption coefficient of acetone and hydrogen.
3. The relative adsorption coefficients of acetone and water drop with increasing temperature (from 2.7 to 0.9 for acetone, and from 1.9 to 0.9 for water), but the coefficients of hydrogen and propylene do not change over the temperature range 280-310°.

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# EFFECT OF METHOD OF PREPARATION ON THE CATALYTIC PROPERTIES OF TITANIUM DIOXIDE IN REACTIONS OF ETHYL AND ISOPROPYL ALCOHOL AND CYCLOHEXANE

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The present paper is devoted to the effect of the method of preparation of titanium dioxide on its catalytic properties. The paper is one in a series of investigations which we have undertaken on  $\text{TiO}_2$  as a catalyst. The catalysts were tried on reactions of ethyl and isopropyl alcohol and cyclohexane. The apparatus and experimental technique was described in [1]. Three samples of titanium dioxide were prepared in a way similar to catalyst 1 (anatase) of [1], except for the first step. For the three catalysts, this first step was as follows: Catalyst 2 was prepared at room temperature by hydrolysis of titanium tetrachloride with ammonia solution (at the time of precipitation, the medium was weakly acid to litmus) according to the method proposed by Bischoff [2]. Catalyst 3 was prepared by adding ammonia to titanium trichloride, to the complete precipitation of the hydroxide of trivalent titanium. The precipitation was carried out at room temperature, and with shaking. The precipitate was washed free of chlorine ions with distilled water. As the precipitate is washed, the color changes from violet (the hydroxide of trivalent titanium) to white (the hydroxide of tetravalent titanium). The white titanium hydroxide prepared in this way was initially dried in air, and then subjected to the treatment described in [1]. Catalyst 4 was prepared at room temperature from the hydrolysis of orthoethyltitanate by distilled water, with shaking. All the catalysts were prepared and used in the form of particles with the dimension  $l = 1.5$  mm, diameter 1 mm (catalyst 4 was used in the form of a powder).

Reactions of ethyl alcohol on different titanium dioxide samples. With ethyl alcohol, three reactions proceed on the catalytic surface of all the samples — dehydrogenation, dehydration of the alcohol, and hydrogenization of ethylene, as has been described in the papers by Rubinstein, Kulikov [3] and Engelder [4] on ethyl alcohol reactions

TABLE 1. Reactions of Ethyl Alcohol on the Partially Carbonated Surface of Catalyst 1 (volume of catalyst 10 ml; weight 7.1 gm; length of layer 4.5 cm; alcohol introduction rate 0.193 ml/min;  $\epsilon_{\text{H}_2} = 22,800$  cal/M;  $\epsilon_{\text{H}_2\text{O}} = 25,000$  cal/M;  $\epsilon_{\text{hydr}} = 21,000$  cal/M). For details of calculating  $\bar{m}$ , see note to Table 8.

| Temperature, °C | V of gas, ml/min | Dehydrogenation of alcohol |            |                          |            | Dehydration of alcohol    |            |                          |            | Hydrogenation of ethylene |            |                          |            | Gas analysis, % |                |      |
|-----------------|------------------|----------------------------|------------|--------------------------|------------|---------------------------|------------|--------------------------|------------|---------------------------|------------|--------------------------|------------|-----------------|----------------|------|
|                 |                  | $\bar{m}$ , min. ml · cat  | $\log k_0$ | $\epsilon \cdot 10^{-3}$ | $\log k_0$ | $\bar{m}$ , min. ml · cat | $\log k_0$ | $\epsilon \cdot 10^{-3}$ | $\log k_0$ | $\bar{m}$ , min. ml · cat | $\log k_0$ | $\epsilon \cdot 10^{-3}$ | $\log k_0$ | unsat.          | H <sub>2</sub> | sat. |
| 299             | 6,2              | 0,20                       | 7,95       | 2,87                     | 0,40       | 9,15                      | 2,73       | 0,17                     | 7,33       | 2,89                      | 64,0       | 32,0                     | 27,2       |                 |                |      |
| 307             | 8,1              | 0,25                       | 8,01       | 2,84                     | 0,52       | 9,16                      | 2,73       | 0,21                     | 7,32       | 2,89                      | 64,2       | 31,5                     | 25,9       |                 |                |      |
| 315             | 11,4             | 0,33                       | 8,00       | 2,85                     | 0,76       | 9,16                      | 2,73       | 0,24                     | 7,13       | 2,97                      | 67,0       | 29,0                     | 21,0       |                 |                |      |
| 325             | 18,0             | 0,56                       | 8,07       | 2,82                     | 1,19       | 9,22                      | 2,71       | 0,43                     | 7,33       | 2,89                      | 66,5       | 31,0                     | 23,9       |                 |                |      |
| 329             | 19,6             | 0,57                       | 8,04       | 2,84                     | 1,39       | 9,22                      | 2,71       | 0,41                     | 7,21       | 2,94                      | 71,2       | 29,0                     | 20,9       |                 |                |      |
| 335             | 19,8             | 0,59                       | 7,97       | 2,86                     | 1,30       | 9,41                      | 2,74       | 0,39                     | 7,21       | 2,94                      | 65,7       | 29,8                     | 19,7       |                 |                |      |
| 340             | 25,0             | 0,76                       | 8,03       | 2,84                     | 1,67       | 9,14                      | 2,73       | 0,57                     | 7,31       | 2,89                      | 67,0       | 30,6                     | 22,8       |                 |                |      |
| Mean            |                  |                            | 8,01       | 2,84                     |            | 9,17                      | 2,73       |                          | 7,26       | 2,91                      |            |                          |            |                 |                |      |
| Mean            |                  | $k_0 = 1,02 \cdot 10^8$    |            |                          |            | $k_0 = 1,05 \cdot 10^9$   |            |                          |            | $k_0 = 1,8 \cdot 10^7$    |            |                          |            |                 |                |      |

TABLE 2. Reactions of Ethyl Alcohol on the Partially Carbonated Surface of Catalyst 2 (volume of catalyst 6.5 ml; weight 4.5 gm; length of layer 3.0 cm; alcohol introduction rate 0.193 ml/mol;  $\epsilon_{H_2} = 20,400$  cal/M;  $\epsilon_{H_2O} = 25,400$  cal/M;  $\epsilon_{hydr} = 24,200$  cal/M)

| Temperature, °C | V of gas, ml/min | Dehydrogenation of alcohol                             |            |                          | Dehydration of alcohol                                 |            |                          | Hydrogenation of ethylene                              |            |                          | Gas analysis, % |                |      |
|-----------------|------------------|--|------------|--------------------------|--|------------|--------------------------|--|------------|--------------------------|-----------------|----------------|------|
|                 |                  | $\frac{m}{ml \cdot min} \cdot \frac{ml}{ml \cdot cat}$ | $\log k_0$ | $\epsilon \cdot 10^{-3}$ | $\frac{m}{ml \cdot min} \cdot \frac{ml}{ml \cdot cat}$ | $\log k_0$ | $\epsilon \cdot 10^{-3}$ | $\frac{m}{ml \cdot min} \cdot \frac{ml}{ml \cdot cat}$ | $\log k_0$ | $\epsilon \cdot 10^{-3}$ | unsat.          | H <sub>2</sub> | sat. |
| 334             | 6,5              | 0,80   | 7,44       | 2,74                     | 0,40   | 8,75       | 2,90                     | 0,22   | 8,06       | 3,0                      | 40,1            | 81,0           | 24,0 |
| 346             | 10,0             | 1,25   | 7,32       | 2,79                     | 0,61   | 8,73       | 2,90                     | 0,35   | 8,10       | 2,98                     | 40,0            | 81,3           | 22,8 |
| 352             | 9,3              | 0,90   | 7,17       | 2,84                     | 0,78   | 8,77       | 2,90                     | 0,31   | 7,94       | 3,05                     | 54,5            | 62,9           | 21,3 |
| 371             | 24,2             | 2,40   | 7,24       | 2,82                     | 1,86   | 8,89       | 2,86                     | 0,69   | 8,04       | 3,0                      | 56,9            | 34,5           | 21,3 |
| 380             | 24,8             | 2,80   | 7,28       | 2,80                     | 1,93   | 8,78       | 2,89                     | 0,98   | 8,03       | 2,98                     | 50,5            | 73,7           | 25,9 |
| 404             | 30,0             | 3,54   | 7,19       | 2,84                     | 2,06   | 8,56       | 2,96                     | 1,17   | 7,83       | 3,07                     | 44,6            | 76,7           | 25,2 |
| Mean            |                  |  | 7,27       | 2,81                     |  | 8,75       | 2,90                     |  | 8,02       | 3,01                     |                 |                |      |
| Mean            |                  | $k_0 = 1,9 \cdot 10^7$                                 |            |                          | $k_0 = 5,6 \cdot 10^8$                                 |            |                          | $k_0 = 1,0 \cdot 10^8$                                 |            |                          |                 |                |      |

TABLE 3. Reactions of Ethyl Alcohol on the Partially Carbonated Surface of Catalyst 3 (volume of catalyst 7 ml; weight 5 gm; length of layer 3.2 cm; alcohol introduction rate 0.193 ml/min;  $\epsilon_{H_2} = 9400$  cal/M;  $\epsilon_{H_2O} = 6900$  cal/M;  $\epsilon_{hydr} = 13,00$  cal/M).

| Temperature, °C | V of gas, ml/min | Dehydrogenation of alcohol                             |          |                          | Dehydration of alcohol                                 |            |                          | Hydrogenation of ethylene                              |            |                          | Gas analysis, % |        |      |
|-----------------|------------------|--|----------|--------------------------|--|------------|--------------------------|--|------------|--------------------------|-----------------|--------|------|
|                 |                  | $\frac{m}{ml \cdot min} \cdot \frac{ml}{ml \cdot cat}$ | $\log k$ | $\epsilon \cdot 10^{-3}$ | $\frac{m}{ml \cdot min} \cdot \frac{ml}{ml \cdot cat}$ | $\log k_0$ | $\epsilon \cdot 10^{-3}$ | $\frac{m}{ml \cdot min} \cdot \frac{ml}{ml \cdot cat}$ | $\log k_0$ | $\epsilon \cdot 10^{-3}$ | H <sub>2</sub>  | unsat. | sat. |
| 392             | 17,0             | 1,40   | 3,3      | 3,01                     | 2,01   | 2,56       | 2,7                      | 0,74   | 4,15       | 3,01                     | 45,2            | 82,7   | 30,7 |
| 409             | 17,8             | 1,20   | 3,10     | 3,04                     | 2,20   | 2,55       | 2,7                      | 0,93   | 4,14       | 3,04                     | 47,3            | 86,7   | 36,4 |
| 426             | 20,6             | 1,41   | 3,09     | 3,04                     | 2,53   | 2,56       | 2,7                      | 1,10   | 4,11       | 3,04                     | 48,0            | 86,1   | 37,6 |
| 439             | 22,6             | 1,70   | 3,12     | 3,02                     | 2,71   | 2,55       | 2,7                      | 1,40   | 4,13       | 3,02                     | 52,8            | 86,5   | 43,5 |
| 457             | 30,7             | 2,36   | 3,18     | 2,95                     | 3,91   | 2,65       | 2,6                      | 1,90   | 4,08       | 2,95                     | 53,7            | 85,9   | 43,3 |
| Mean            |                  |  | 3,13     | 3,01                     |  | 2,57       | 2,7                      |  | 4,12       | 3,01                     |                 |        |      |
| Mean            |                  | $k_0 = 1,4 \cdot 10^3$                                 |          |                          | $k_0 = 3,7 \cdot 10^2$                                 |            |                          | $k_0 = 1,3 \cdot 10^4$                                 |            |                          |                 |        |      |

on titanium dioxide prepared in other ways. In calculating the activation energy of the first two reactions, we took account of the quantity of ethane formed. All four catalysts likewise promote the formation of ethylacetate (up to 2%). Tables 1-4 give the data for calculating the activation energy of the dehydrogenation and dehydration of ethyl alcohol, and the hydrogenation of ethylene. The activation energies were calculated from Arrhenius' equation, taking as the rate constant the values of  $\bar{m}$  (see Tables 1-4) for hydrogen,  $C_2H_4$  and  $C_2H_6$ .

Reactions of isopropyl alcohol. On all the samples of catalyst, isopropyl alcohol undergoes transformations similar to those described in [1], i.e., the accumulation of carbon deposits leads, in all cases, to the observation that in the first 20 min the dehydration rate of the alcohol increases continuously, while the rate of dehydrogenation falls continuously. At the same time, the total activity of each one of the four catalysts maintains itself constant. Tables 5 and 6 give data for the reactions of isopropyl alcohol on catalysts 2, 3, and 4. The reactions of isopropyl alcohol on catalyst 1 (anatase) are described in detail in [1] and [5], here only the activation energy  $\epsilon$  is given, without the corresponding tables: On the uncarbonated surface of the anatase,  $\epsilon_{H_2} = 11,9$  kilo-cal/M; mean  $k_0 = 1,9 \cdot 10^5$ , on the partially carbonated surface,  $\epsilon_{H_2} = 9,0$  kilo-cal/M; mean  $k_0 = 1,0 \cdot 10^4$ , also on the partially carbonated surface,  $\epsilon_{H_2} = 24,4$  kilo-cal/M; mean  $k_0 = 4,5 \cdot 10^9$ , on the completely carbonated surface,  $\epsilon_{H_2} = 22,9$  kilo-cal/M; mean  $k_0 = 3,7 \cdot 10^9$ .

TABLE 4. Reactions of Ethyl Alcohol on the Partially Carbonated Surface of Catalyst 4 (volume of catalyst 7 ml; weight 4.9 gm; length of layer 3.3 cm; alcohol introduction rate 0.193 ml/min;  $\epsilon_{H_2} = 12,400$  cal/M;  $\epsilon_{H_2O} = 12,500$  cal/M;  $\epsilon_{hydr} = 16,800$  cal/M)

| Temperature, °C | V of gas, ml/min | Dehydrogenation of alcohol                             |            |   | Dehydration of alcohol                                 |            |   | Hydrogenation of ethylene                              |            |   | Gas analysis, % |        |       |
|-----------------|------------------|--|------------|---|--|------------|---|--|------------|---|-----------------|--------|-------|
|                 |                  | $\frac{m}{ml \cdot min} \cdot \frac{ml}{ml \cdot cat}$ | $\log k_0$ | $\frac{\epsilon}{\log k_0} \cdot 10^{-3}$ | $\frac{m}{ml \cdot min} \cdot \frac{ml}{ml \cdot cat}$ | $\log k_0$ | $\frac{\epsilon}{\log k_0} \cdot 10^{-3}$ | $\frac{m}{ml \cdot min} \cdot \frac{ml}{ml \cdot cat}$ | $\log k_0$ | $\frac{\epsilon}{\log k_0} \cdot 10^{-3}$ | H <sub>2</sub>  | unsat. | sat.  |
| 340             | 12.1             | 0.48   | 4.08       | 3.04                                      | 1.54   | 4.63       | 2.70                                      | 0.34   | 5.36       | 3.14                                      | 27.10           | 87.10  | 19.10 |
| 357             | 18.7             | 0.65   | 4.11       | 3.02                                      | 2.40   | 4.72       | 2.65                                      | 0.44   | 5.49       | 3.07                                      | 24.25           | 89.80  | 16.80 |
| 374             | 22.2             | 0.73   | 4.06       | 3.06                                      | 2.54   | 4.62       | 2.71                                      | 0.56   | 5.42       | 3.10                                      | 23.00           | 80.30  | 17.80 |
| 383             | 23.0             | 0.80   | 4.03       | 3.08                                      | 2.74   | 4.59       | 2.73                                      | 0.67   | 5.43       | 3.10                                      | 24.50           | 83.60  | 20.60 |
| 398             | 26.8             | 1.26   | 4.10       | 3.03                                      | 3.54   | 4.62       | 2.71                                      | 1.05   | 5.49       | 3.07                                      | 33.05           | 92.6   | 27.40 |
| Mean            |                  |  | 4.07       | 3.05                                      |  | 4.64       | 2.70                                      |  | 5.44       | 3.10                                      |                 |        |       |
| Mean            |                  | $k_0 = 1.2 \cdot 10^4$                                 |            |   | $k_0 = 4.4 \cdot 10^4$                                 |            |   | $k_0 = 2.7 \cdot 10^5$                                 |            |   |                 |        |       |

TABLE 5. Dehydrogenation and Dehydration of Isopropyl Alcohol on the Partially Carbonated (2.0) Surface, and Dehydration on the Completely Carbonated Catalyst 2 (volume of catalyst 6.5 ml; weight 4.5 gm; length of layer 3.0 cm; alcohol introduction rate 0.263 ml/min;  $\epsilon_{H_2O} = 15.3$  kilo-cal/M;  $k_0 = 6.9 \cdot 10^5$ ;  $\epsilon_{H_2} = 10.4$  kilo-cal/M;  $k_0 = 2.2 \cdot 10^4$ ;  $\epsilon_{H_3O} = 9.1$  kilo-cal/M;  $k_0 = 9.1 \cdot 10^3$ )

| Temperature, °C | V of gas, ml/min | Gas analysis, % |                |      | Dehydration  |            |   | Dehydrogenation  |            |   | Dehydration  |            |   |
|-----------------|------------------|-----------------|----------------|------|--|------------|---|--|------------|---|--|------------|---|
|                 |                  | unsat.          | H <sub>2</sub> | sat. | $\frac{m}{ml \cdot min} \cdot \frac{ml}{ml \cdot cat}$ | $\log k_0$ | $\frac{\epsilon}{\log k_0} \cdot 10^{-3}$ | $\frac{m}{ml \cdot min} \cdot \frac{ml}{ml \cdot cat}$ | $\log k_0$ | $\frac{\epsilon}{\log k_0} \cdot 10^{-3}$ | $\frac{m}{ml \cdot min} \cdot \frac{ml}{ml \cdot cat}$ | $\log k_0$ | $\frac{\epsilon}{\log k_0} \cdot 10^{-3}$ |
| 253             | 9.7              | 23.6            | 78.5           | 3.3  | 0.36   | 5.91       | 2.59                                      | 1.19   | 4.39       | 2.77                                      | 1.51   | 3.96       | 2.29                                      |
| 270             | 6.9              | 43.5            | 58.8           | 3.3  | 0.24   | 5.54       | 2.76                                      | 1.00   | 4.18       | 2.49                                      | 1.09   | 3.72       | 2.44                                      |
| 281             | 17.9             | 33.8            | 69.7           | 6.1  | 0.95   | 6.01       | 2.55                                      | 1.95   | 4.40       | 2.36                                      | 2.80   | 4.04       | 2.26                                      |
| 290             | 18.4             | 29.6            | 72.2           | 3.0  | 0.85   | 5.88       | 2.60                                      | 2.08   | 4.36       | 2.39                                      | 2.88   | 4.00       | 2.28                                      |
| 304             | 22.6             | 35.7            | 56.3           | 2.6  | 1.26   | 5.90       | 2.60                                      | 1.99   | 4.24       | 2.42                                      | 3.54   | 4.00       | 2.28                                      |
| 310             | 21.9             |                 |                |      |  |            |   |  |            |   | 3.42   | 3.94       | 2.30                                      |
| 316             | 25.4             |                 |                |      |  |            |   |  |            |   | 3.96   | 3.98       | 2.28                                      |
| Mean            |                  |                 |                |      |  | 5.84       | 2.62                                      |  | 4.34       | 2.40                                      |  | 3.96       | 2.28                                      |

Dehydrogenation of cyclohexane. All samples of titanium dioxide catalyst facilitate smoothly running dehydrogenation of cyclohexane. The gaseous reaction products consist solely of hydrogen. In the liquid catalyzate, the content of unsaturated compounds does not exceed 0.5%. After every experiment, the catalyst was regenerated for 30-40 min in a stream of air, at a temperature exceeding the experimental temperature by 40-50°[1,5]. The data from the dehydrogenation of cyclohexane are given in Table 7.

Table 8 shows the reactions, the surface characteristics, the activation energy etc., for all four samples of catalyst. It is obvious that the method of preparing the catalyst influences the catalytic properties substantially, as is shown both by the values of the activation energy for the general reaction, and by the values of the exponential term. It is clear from Table 8 that the value of  $\epsilon/\log k_0$  remains approximately constant, i.e., for all the reactions recounted in the paper, the dehydrogenation of alcohols and hydrocarbons and the hydrogenation of the olefin on the one hand, and the dehydration of the alcohol on the other, it is justifiable to assume the logarithmic relationship  $\log k_0 = a + b/\epsilon$  [6], where  $k_0$  is the exponential term in the Arrhenius equation,  $\epsilon$  is the activation energy of the reaction, and  $a$  and  $b$  are constants.

TABLE 6. Dehydration of Isopropyl Alcohol on Carbonated Catalyst Surface

| Catalyst 3   |  |  |  | Catalyst 4   |  |  |  |
|--|--|--|--|--|--|--|--|
| (volume of catalyst 7 ml; weight 5 gm; length of layer 3.2 cm; alcohol introduction rate 0.236 ml/min; $\epsilon$ H <sub>2</sub> O = 26.2 kilo-cal/M; $k_0 = 1.02 \cdot 10^{10}$ ) |  |  |  | (volume of catalyst 7 ml; weight 4.9 gm; length of layer 3.3 cm; alcohol introduction rate 0.263 ml/min; $\epsilon$ H <sub>2</sub> O = 17.2 kilo-cal/M; $k_0 = 2.8 \cdot 10^7$ ) |  |  |  |

| Temperature, °C | m, ml/min · ml · cat | log $k_0$ | $\frac{\epsilon}{\log k_0} \cdot 10^{-3}$ | Temp., °C | m, ml/min · ml · cal | log $k_0$ | $\frac{\epsilon}{\log k_0} \cdot 10^{-3}$ |
|-----------------|----------------------|-----------|---|-----------|----------------------|-----------|---|
| 294             | 0,86                 | 10,04     | 2,61                                      | 233       | 0,96                 | 7,40      | 2,32                                      |
| 300             | 1,37                 | 10,02     | 2,67                                      | 238       | 1,54                 | 7,54      | 2,28                                      |
| 313             | 2,33                 | 10,13     | 2,68                                      | 244       | 1,64                 | 7,48      | 2,30                                      |
| 320             | 3,03                 | 10,13     | 2,68                                      | 247       | 2,05                 | 7,55      | 2,28                                      |
| 324             | 3,80                 | 10,18     | 2,58                                      | 255       | 2,33                 | 7,49      | 2,30                                      |
|                 |                      |           |   | 260       | 2,74                 | 7,49      | 2,30                                      |
|                 |                      |           |   | 303       | 4,23                 | 7,17      | 2,40                                      |
|                 | Mean                 | 10,10     | 2,54                                      |           | Mean                 | 7,45      | 2,31                                      |

TABLE 7. Dehydrogenation of Cyclohexane on Partially Carbonated Surfaces of Titanium Dioxide-Catalysts

| Catalyst 2  |  |  |  | Catalyst 3  |  |  |  | Catalyst 4  |  |  |  |
|---|--|--|--|---|--|--|--|---|--|--|--|
| (volume of catalyst 6.3 ml; length of layer 3.0 cm; cyclohexane introduction rate 0.193 ml/min; $\epsilon$ H <sub>2</sub> = 14.7 kilo-cal/M; $k_0 = 5.1 \cdot 10^4$ ) |  |  |  | (volume of catalyst 7 ml; length of layer 3.2 cm; cyclohexane introduction rate 0.193 ml/min; $\epsilon$ H <sub>2</sub> = 21.6 kilo-cal/M; $k_0 = 1.3 \cdot 10^6$ ) |  |  |  | (volume of catalyst 7 ml; length of layer 3.3 cm; cyclohexane introduction rate 0.193 ml/min; $\epsilon$ H <sub>2</sub> = 15.0 kilo-cal/M; $k_0 = 3.5 \cdot 10^4$ ) |  |  |  |

| Temperature, °C | m, ml/min · ml · cat | log $k_0$ | $\frac{\epsilon}{\log k_0} \cdot 10^{-3}$ | Temperature, °C | m, ml/min · ml · cat | log $k_0$ | $\frac{\epsilon}{\log k_0} \cdot 10^{-3}$ | Temperature, °C | m, ml/min · ml · cat | log $k_0$ | $\frac{\epsilon}{\log k_0} \cdot 10^{-3}$ |
|-----------------|----------------------|-----------|---|-----------------|----------------------|-----------|---|-----------------|----------------------|-----------|---|
| 460             | 1,71                 | 4,61      | 3,19                                      | 480             | 0,68                 | 6,11      | 3,54                                      | 454             | 1,07                 | 4,65      | 3,23                                      |
| 467             | 2,39                 | 4,76      | 3,09                                      | 490             | 0,83                 | 6,11      | 3,54                                      | 472             | 1,16                 | 4,54      | 3,30                                      |
| 482             | 3,05                 | 4,74      | 3,10                                      | 504             | 1,20                 | 6,16      | 3,50                                      | 474             | 1,37                 | 4,54      | 3,30                                      |
| 503             | 3,62                 | 4,71      | 3,12                                      | 513             | 1,30                 | 6,11      | 3,54                                      | 479             | 1,53                 | 4,54      | 3,30                                      |
| 523             | 4,86                 | 4,72      | 3,12                                      | 518             | 1,36                 | 6,10      | 3,54                                      | 486             | 1,68                 | 4,53      | 3,30                                      |
|                 |                      |           |   |                 |                      |           |   | 496             | 1,85                 | 4,41      | 3,36                                      |
|                 |                      |           |   |                 |                      |           |   | 505             | 2,78                 | 4,54      | 3,30                                      |
|                 | Mean                 | 4,71      | 3,12                                      |                 | Mean                 | 6,12      | 3,53                                      |                 | Mean                 | 4,54      | 3,30                                      |

Figures 1 and 2 show the range over which this logarithmic relationship is observed. The results of this paper will be used in a subsequent communication, dealing with the binding energy.

TABLE 8. Effect of Method of Preparation of  $\text{TiO}_2$  Catalyst on Activation Energy

| Surface state of catalyst | Reaction                             | $\epsilon$ , kilo-cal/M |      |      |      | $k_0$            |                  |                     |                  | $\epsilon / \log k_0 \cdot 10^3$ |      |      |      |
|---------------------------|--------------------------------------|-------------------------|------|------|------|------------------|------------------|---------------------|------------------|----------------------------------|------|------|------|
|                           |                                      | catalyst                |      |      |      | catalyst         |                  |                     |                  | catalyst                         |      |      |      |
|                           |                                      | 1                       | 2    | 3    | 4    | 1                | 2                | 3                   | 4                | 1                                | 2    | 3    | 4    |
| Part                      | Dehydrogenation of ethyl alcohol     | 22.8                    | 20.4 | 9.4  | 12.4 | $1.0 \cdot 10^8$ | $1.9 \cdot 10^7$ | $1.4 \cdot 10^3$    | $1.2 \cdot 10^4$ | 2.84                             | 2.81 | 3.01 | 3.05 |
| Part                      | Dehydration of ethyl alcohol         | 25.0                    | 25.4 | 6.9  | 12.5 | $1.5 \cdot 10^8$ | $5.6 \cdot 10^8$ | $3.7 \cdot 10^2$    | $4.4 \cdot 10^4$ | 2.73                             | 2.90 | 2.70 | 2.70 |
| Full                      | Dehydration of isopropyl alcohol     | 22.9                    | 9.1  | 26.2 | 17.2 | $3.7 \cdot 10^9$ | $9.1 \cdot 10^4$ | $1.0 \cdot 10^{10}$ | $2.8 \cdot 10^7$ | 2.39                             | 2.28 | 2.54 | 2.31 |
| Part                      | Hydrogenation of ethylene            | 21.2                    | 24.2 | 13.0 | 16.8 | $1.8 \cdot 10^7$ | $1.0 \cdot 10^8$ | $1.3 \cdot 10^4$    | $2.7 \cdot 10^5$ | 2.91                             | 3.01 | 3.01 | 3.10 |
| Part                      | Dehydrogenation of cyclohexane       | 19.0                    | 14.7 | 21.6 | 15.0 | $8.7 \cdot 10^5$ | $5.1 \cdot 10^4$ | $1.3 \cdot 10^6$    | $3.5 \cdot 10^4$ | 3.20                             | 3.12 | 3.53 | 3.30 |
| Part                      | Dehydrogenation of isopropyl alcohol | 9.1                     | 10.4 | —    | —    | $1.0 \cdot 10^4$ | $2.2 \cdot 10^4$ | —                   | —                | 2.24                             | 2.40 | —    | —    |
| Part                      | Dehydration of isopropyl alcohol     | 24.4                    | 15.3 | —    | —    | $4.5 \cdot 10^9$ | $6.9 \cdot 10^5$ | —                   | —                | 2.53                             | 2.62 | —    | —    |
| None                      | Dehydrogenation of isopropyl alcohol | 11.9                    | —    | —    | —    | $1.9 \cdot 10^5$ | —                | —                   | —                | 2.25                             | —    | —    | —    |
| Full                      | Dehydrogenation of cyclohexane       | 25.2                    | —    | —    | —    | $4.9 \cdot 10^7$ | —                | —                   | —                | 2.71                             | —    | —    | —    |
| Part                      | Dehydrogenation of propyl alcohol    | 19.4                    | —    | —    | —    | $2.3 \cdot 10^6$ | —                | —                   | —                | 3.05                             | 2.73 | 2.96 | 2.89 |
| Part                      | Dehydration of n-propyl alcohol      | 12.1                    | —    | —    | —    | $4.5 \cdot 10^4$ | —                | —                   | —                | 2.60                             | —    | —    | —    |

Note; Tables 1-5. Since the secondary ethylene hydrogenation reaction leads to a reduction in the observed volume  $\bar{v}$  of the gaseous reaction products, to find from this volume the actual quantities of  $\text{C}_2\text{H}_4$  and  $\text{H}_2$ , formed originally, the percentage content of  $\text{C}_2\text{H}_6$  is added to the percentage content of  $\text{C}_2\text{H}_4$  and  $\text{H}_2$  in the evolved gas  $\bar{v}$ . Tables 1-5 do not give the  $\text{CO}_2$  content, which varies from 0.1 to 5%. For catalyst 2 (full) the gaseous products consisted only of propylene (Table 5).

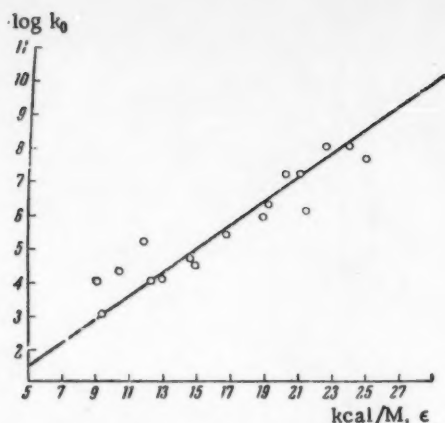


Fig. 1. Dehydrogenation of alcohols and hydrocarbons, hydrogenation of ethylene.

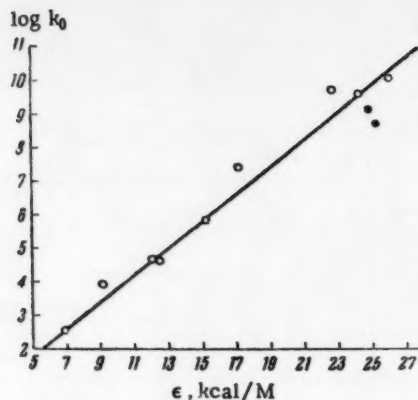


Fig. 2. Dehydration of alcohols.

1. Changing the method of preparation substantially changes the catalytic properties of titanium dioxide, as is shown by the values of the activation energy, and the exponential terms in the Arrhenius equation for this type of reaction.
2. All the reactions given confirm the logarithmic dependence between the constants of the Arrhenius equation.

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ESTERS OF PHOSPHORIC AND THIOPHOSPHORIC ACIDS  
CONTAINING HETEROCYCLIC RADICALS  
COMMUNICATION 3. COMPOUNDS WITH TETRAHYDROFURFURYL RADICALS







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Translated from *Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk*,  
No. 1, pp. 51-55, January, 1961  
Original article submitted September 5, 1959

One of us and Lugovkin [1] have already prepared the ethyl ether of  $\alpha$ -tetrahydrofurfurylphosphinic acid by the action of sodium diethylphosphate and triethylphosphite on  $\alpha$ -bromomethyltetrahydrofuran. Esters of phosphoric and phosphorous acids with tetrahydrofurfuryl radicals were unknown until now.

Some representatives of this group of esters are described in the present communication. We synthesized diethyl-, diisopropyl-, di-n-butyl-, and isobutyltetrahydrofurfurylphosphates, and studied some of their properties. Their physical constants are given in Table 1.

TABLE 1.

| Formula  | B.p., °C<br>(mm Hg)  | $n_D^{20}$ | $d_4^{20}$ | MR    |                     | Yield,<br>%   |
|--|----------------------|------------|------------|-------|---------------------|---------------|
|  |                      |            |            | found | calc.               |               |
|  $\text{CH}_2\text{O}-\text{P}(=\text{O})(\text{OC}_2\text{H}_5)_2$  | 132-133<br>(2,5)     | 1,4375     | 1,1366     | 54,94 | 55,20               | 60            |
|  $\text{CH}_2\text{O}-\text{P}(=\text{O})(\text{OC}_3\text{H}_7)_2$ | 141-142<br>(3)       | 1,4352     | 1,0794     | 64,37 | 64,44               | 43,3          |
|  $\text{CH}_2\text{O}-\text{P}(=\text{O})(\text{OC}_4\text{H}_9)_2$ | 150-152<br>(2)       | 1,4415     | 1,0614     | 73,27 | 73,67               | 39,5          |
|  $\text{CH}_2\text{O}-\text{P}(=\text{O})(\text{OC}_4\text{H}_9)_2$ | 145-147<br>(2,5)     | 1,4388     | 1,0508     | 73,61 | 73,67               | 40            |
|  $\left(\text{CH}_2\text{O}\right)_2-\text{POH}_2^*$                | 151-152,5<br>(1,5-2) | 1,4733     | 1,2050     | 58,25 | 60,21**<br>58,13*** | 46,1          |
|  $\left(\text{CH}_2\text{O}\right)_3-\text{P}$                      | 170-171<br>(1)       | 1,4838     | 1,1582     | 82,52 | 82,86               | 51,7;<br>44,5 |

\* Literature data [2]: b. p. 134-136° (0.06 mm);  $n_D^{20}$  1.4735;  $d_4^{20}$  1.2046.

\*\* For trivalent phosphorus.






\*\*\* For pentavalent phosphorus.

The esters of phosphoric acid containing a tetrahydrofurfuryl radical appeared to be physiologically active. Experiments carried out by Neklesova on barn weevils and mice showed that these compounds are rather powerful insecticides and possess toxic properties (Table 2).

We thought it would also be interesting to synthesize the esters of phosphorous acid containing the tetrahydrofurfuryl radical, and to study their properties. We prepared tritetrahydrofurfurylphosphite and ditetrahydrofurfuryl-

phosphite (Table 2). The former was obtained in two ways: Either by the action of phosphorus trichloride on tetrahydrofurfuryl alcohol in the presence of a base, or by trans-esterification of triethyl phosphite in the presence of phosphoric acid. Ditetrahydrofurfurylphosphite was prepared by the action of phosphorus trichloride on tetrahydrofurfuryl alcohol in ethereal solution. Tikhii and Trukhlik [2] obtained this product by trans-esterification of diethylphosphite. The constants of our phosphite are very close to those given by the Czeck authors.

TABLE 2.

| Formula   | Concentration of the solution, %          | Mortality of barn weevil in 7 days                  |   |
|---|---|---|---|
|  $\text{CH}_2\text{--O--P(=O)(C}_2\text{H}_5)_2$           | 0,01<br>0,02<br>0,05<br>0,1<br>0,5<br>1,0 | 49<br>44<br>58<br>76<br>100 (3 days)<br>100 (1 day) | $LD_{50} \sim$<br>$\sim 4 \text{ mg/kg}$<br>$LD_{100} \sim$<br>$\sim 5 \text{ mg/kg}$ |
|  $\text{CH}_2\text{--O--P(=O)(OC}_4\text{H}_9\text{-i})_2$ | 0,1<br>0,5<br>1,0                         | 54<br>76<br>94                                      |   |
|  $\text{CH}_2\text{--O--P(=O)(OC}_4\text{H}_9\text{-i})_2$ | 0,5<br>1,0                                | 72<br>72  |   |
|  $\text{CH}_2\text{--O--P(=O)(OC}_4\text{H}_9\text{-i})_2$ | 0,1<br>0,5<br>1,0                         | 75<br>89<br>96                                      |   |
|  $\text{CH}_2\text{--O--POH}_2$                            | 1,0                                       | 80  |   |

Experiments were carried out on the Arbuzov isomerization of tritetrahydrofurfurylphosphite to phosphinic acid ester at different temperatures. However, it was not possible to obtain the isomerization products in any of the cases studied. At temperatures below 165-170°, there was no reaction, while at temperatures above 180°, the reaction products resinified strongly, and it was not possible to isolate individual compounds. The expected phosphinic ester with a tetrahydrofurfuryl radical could not be obtained by the action of the sodium salt of ditetrahydrofurfurylphosphite on  $\alpha$ -bromomethyltetrahydrofuran in dry ethereal medium.

#### EXPERIMENTAL

**Preparation of diethyl- $\alpha$ -tetrahydrofurfurylphosphate.** A solution of 11.21 g of tetrahydrofurfuryl alcohol and 10.11 g of triethylamine in 50 ml of dry ether was treated at room temperature with 17.4 g diethylphosphoryl chloride diluted with its volume of dry ether. The temperature of the reaction mixture remained practically unchanged. The mixture was heated for 1.5 hr on a water bath. After cooling, the precipitate of triethylamine hydrochloride was filtered off, and the filtrate was distilled in vacuum. Double distillation gave 15.4 g (60%) of a product boiling at 132-133° (2.5 mm);  $n_D^{20}$  1.4375,  $d_4^{20}$  1.1366; found MR 54.94; calculated MR 55.20. It appeared as an almost odorless, colorless, oily liquid, soluble in organic solvents and water. Found: P 13.14%.  $C_9H_{19}O_5P$ . Calculated: P 13.01%.

**Preparation of diisopropyl- $\alpha$ -tetrahydrofurfurylphosphate.** A solution of 9.6 g of tetrahydrofurfuryl alcohol and 8.66 g of triethylamine in dry ether was treated with 17.2 g of diisopropylphosphoryl chloride. The reaction was triggered by the addition of a few crystals of triethylamine hydrochloride. At the beginning, only a turbidity occurred in the mixture. Upon heating on a water bath, the amount of precipitate gradually increased. After 2 hr the reaction was considered to be completed, and the mixture was filtered from the precipitated triethylamine hydrochloride (about 8 g). Distillation of the filtrate gave 10.5 g (43.3%) of a product boiling at 141-142° (3 mm);  $n_D^{20}$  1.4352,  $d_4^{20}$  1.0794; found MR 64.37; calculated MR 64.44. It appeared as an oily liquid resembling the preceding ester, and was soluble in the common organic solvents. In contrast to the preceding product, it was very sparingly soluble in water. Found: C 49.39; H 8.82; P 12.00%.  $C_{11}H_{22}O_5P$ . Calculated: C 49.59; H 8.70; P 11.64%.

Preparation of di-n-butyl- $\alpha$ -tetrahydrofurfurylphosphate. Unlike the preceding esters, this compound was prepared in a solution of dry benzene. A mixture of 7.85 g of tetrahydrofurfuryl alcohol, 7.07 g of triethylamine, and 50 ml of dry benzene was treated with a benzene solution of 16 g of di-n-butylphosphoryl chloride. The mixture became turbid and warmed up slightly. A precipitate was gradually formed upon standing. The reaction mixture was refluxed for 1.5 hr, and treated in the same way as in the foregoing experiments. Yield, 8.1 g (39.5%); b. p. 150-152.5° (2 mm);  $n_D^{20}$  1.4415,  $d_4^{20}$  1.0614; found MR 73.27; calculated MR 73.67. The physical properties of this product were analogous to those of the preceding substances. Found: P 10.92%.  $C_{13}H_{27}O_5P$ . Calculated: P 10.53%.

Preparation of diisobutyl- $\alpha$ -tetrahydrofurfurylphosphate. The procedure was the same as in the preceding experiment. The amounts used were: 11.22 g of tetrahydrofurfuryl alcohol, 10.12 g of triethylamine, and 22.86 g of the acid chloride. The mixture was refluxed for 2 hr. Vacuum distillation gave 11.8 g (40%) of the ester, b. p. 145-147° (2.5 mm);  $n_D^{20}$  1.4388,  $d_4^{20}$  1.0508; found MR 73.61; calculated MR 73.67. Found: P 10.22%.  $C_{13}H_{27}O_5P$ . Calculated: P 10.53%.

Preparation of tritetrahydrofurfurylphosphate. To synthesize this compound by the action of phosphorus trichloride on tetrahydrofurfuryl alcohol, a solution of 33.62 g of tetrahydrofurfuryl alcohol and 23.71 g of dry pyridine in 100 ml of absolute ether was treated dropwise, and while cooling with ice, with 13.74 g of freshly distilled phosphorus trichloride diluted with its volume of ether. The addition of the first drops of phosphorus trichloride was already accompanied by the separation of pyridine hydrochloride. After all the phosphorus trichloride had been added, the mixture was stirred for a further period of half an hour, and allowed to stand at room temperature overnight. The precipitate was filtered off, and the filtrate submitted to vacuum distillation from an Arbuzov flask. The result of a double distillation was 21.7 g (51.7%) of a product boiling at 180-184° (1.5-2 mm);  $n_D^{20}$  1.4842,  $d_4^{20}$  1.1595; found: MR 82.48; calculated MR 82.86. Found: P 9.44, 9.50%.  $C_{15}H_{27}O_6P$ . Calculated: P 9.27%. This product appeared as a thick colorless liquid soluble in organic solvents and having the properties characteristic for phosphites: It reacted with cuprous iodide with evolution of heat (a thick uncrystallizable mass being formed), as well as with water and sulfur (evolution of heat). It was not possible to isolate the thiophosphate in a pure state, as it decomposed strongly upon distillation in vacuum (1-1.5 mm).

To synthesize the same compound by trans-esterification of triethylphosphite, 33.62 g of tetrahydrofurfuryl alcohol, 16.61 g of triethylphosphite, and one drop of concentrated phosphoric acid were heated in an Arbuzov flask on a Wood bath at 135-145°. Ethyl alcohol distilled over, rapidly at first, and then more slowly. The temperature of the bath was gradually raised to 170°. The total amount of alcohol obtained was 11.9 g (theoretical amount: 13.8 g). After several distillations, 14.9 g (44.5%) of the phosphite was obtained, b. p. 170-171° (1 mm);  $n_D^{20}$  1.4838,  $d_4^{20}$  1.1582; found MR 82.52; calculated MR 82.86.

Experiments on the isomerization of tritetrahydrofurfurylphosphate. A mixture of 5.5 g of the phosphite and 2.72 g of  $\alpha$ -bromomethyltetrahydrofuran (1 mole per mole of ester) was heated in a sealed tube at 165-170° for 6 hr. Distillation of the reaction mixture gave 1.75 g of the starting bromide [b. p. 63° (14 mm);  $n_D^{20}$  1.4790], and 3.2 g of a fraction boiling at 170-195° (1 mm);  $n_D^{20}$  1.4805 (impure starting ester). About 2 g of a thick yellow mass remained in the distilling flask.

A mixture of 20.5 g of the phosphite and 10 g of  $\alpha$ -bromomethyltetrahydrofuran was heated in a sealed tube at 180-200° for 4 hr. The contents of the tube darkened and shrunk. Distillation of the reaction products gave 7.2 g of impure starting bromide, b. p. 64-70° (13 mm);  $n_D^{20}$  1.4690 [after redistillation, b. p. 61-62° (13 mm);  $n_D^{20}$  1.4710], and about 2 g of a fraction boiling at 110-135° (14 mm);  $n_D^{20}$  1.4650. Further heating led to extensive decomposition. About 14 g of a thick brown resin remained in the flask.

Preparation of ditetrahydrofurfurylphosphite. A solution of 33.62 g of tetrahydrofurfuryl alcohol in 100 ml of ether was treated, while cooling in snow, and stirring, with an ethereal solution of 13.71 g of freshly distilled phosphorus trichloride. When the reaction was over, the mixture consisted of two layers: An upper ethereal phase, and a lower oily phase. The reaction mixture was stirred at room temperature for 1 hr. Then the flask was connected to a water pump to ensure the complete removal of hydrogen chloride (3-4 hr; toward the end the flask was heated with hot water). After distilling the reaction product thrice, a substance was obtained which boiled at 151-152.5° (1.5-2 mm);  $n_D^{20}$  1.4733,  $D_4^{20}$  1.2050; found MR 58.25; calculated for pentavalent phosphorus, 58.13; for trivalent phosphorus, 60.21. This substance appeared as an oily, rather thick, colorless liquid soluble in alcohol, ether, benzene, and other organic solvents. It was easily soluble in water, the solution being acid to methyl orange. Found: P 12.42, 12.32%.  $C_{16}H_{19}O_5P$ . Calculated %: P 12.39%.

Reaction of sodium ditetrahydrofurfurylphosphite with  $\alpha$ -bromomethyltetrahydrofuran. The sodium salt was prepared from 9.5 g of ditetrahydrofurfurylphosphorous acid and 0.87 g of metallic sodium in 150 ml of absolute ether. The suspension of the salt was treated with 6.27 g of  $\alpha$ -bromomethyltetrahydrofuran, and the mixture was heated on a water bath with mechanical stirring for 10 hr. Then it was left to stand at room temperature for a long time. The reaction product appeared as two layers: An upper ethereal layer, and a lower viscous, very thick, yellow layer. Distillation of the ethereal layer gave 3.5 g of the starting  $\alpha$ -bromomethyltetrahydrofuran, b. p. 69-73° (16 mm). Further heating led to the decomposition of the remaining product. A very thick polymerized yellow mass remained in the flask.

#### SUMMARY

Esters of phosphoric and phosphorous acids containing tetrahydrofurfuryl radicals were synthesized; some of their properties were studied.

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2. V. Tichy and S. Truchlik, *Chemické Zvesti* 12, 345 (1958).

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

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# SYNTHESIS AND PROPERTIES OF $\beta$ -HALOALLYL COMPOUNDS OF MERCURY

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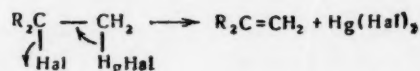
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Attempts to prepare saturated aliphatic compounds of mercury containing a halogen atom in  $\beta$ -position with respect to the mercury atom were unsuccessful [1-7] because of the ease with which the following elimination reaction takes place:



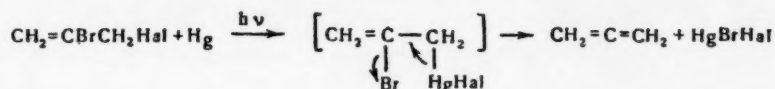
In distinction from saturated  $\beta$ -halosubstituted organic mercury compounds,  $\beta$ -chlorovinyl derivatives of the type  $\text{Cl}-\text{C}=\text{C}-\text{HgX}$  are readily obtained, and are sufficiently stable at ordinary temperature [8].

Earlier, we have described [9-11]  $\gamma, \gamma$ -dichloroallyl derivatives of mercury, and studied the peculiarities of their reactions. In the present paper we describe the preparation of haloallyl organic mercury compounds containing the group  $>\text{C}=\text{CH}_2\text{HgX}$  and report on some of their reactions. The reaction of allyl halides with metallic

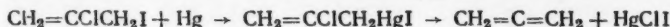


mercury has been chosen for the synthesis of these compounds. The following substances were experimented with:  $\text{CH}_2=\text{CClCH}_2\text{I}$ ,  $\text{CH}_2=\text{CBrCH}_2\text{Br}$ ,  $\text{CH}_2=\text{CBrCH}_2\text{I}$ ,  $\text{CHCl}=\text{CHClCH}_2\text{I}$ ,  $\text{CCl}_2=\text{CClCH}_2\text{Br}$ ,  $\text{CCl}_2=\text{CBrCH}_2\text{I}$ ,  $\text{CCl}_2=\text{CClCH}_2\text{I}$ ,  $\text{BrCCl}_2\text{CCl}=\text{CH}_2$ , and  $\text{CCl}_3\text{CBr}=\text{CH}_2$ .

It appeared that upon reaction with metallic mercury, with or without irradiation with ultraviolet light, 1,2-dibromo-2-propene, and 1-iodo-2-bromo-2-propene, similarly to 1,2-dihaloalkanes, do not form organic mercury compounds; during the reaction, mercury halides and allene are formed. The latter was identified as its adduct with mercuric chloride. It seems that in this case the intermediate organic mercury compound decomposes according to the scheme:

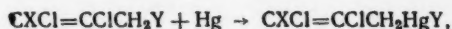


Under analogous conditions, we succeeded in obtaining from 2-chloro-1-iodo-2-propene the comparatively poorly stable  $\beta$ -chloroallyl mercuric iodide, which decomposed upon heating or during storage with evolution of allene



It was impossible to prepare the corresponding mercuric chloride from  $\text{CH}_2=\text{CClCH}_2\text{HgI}$ , either by the action of  $\text{Ag}_2\text{O}$  followed by  $\text{HCl}$ , or by heating with mercuric chloride in ethereal solution. In both cases allene was formed. The reaction of  $\text{CH}_2=\text{CClCH}_2\text{HgI}$  with  $\alpha\text{-C}_{10}\text{H}_7\text{MgBr}$  gave  $\alpha$ -naphthyl mercuric iodide and allene instead of the expected  $\alpha$ -naphthyl-2-chloro-2-propenyl mercury. This reaction illustrates in a convincing manner the lability of the  $\text{C}-\text{Hg}$  bond due to the influence of the chlorine atom in  $\beta$ -position to the mercury atom.

The presence of chlorine atoms in  $\gamma$ -position to the halomercury group stabilizes the molecule of  $\beta$ -haloallylmercury halides. Thus, the reaction of  $\text{CHCl}=\text{CClCH}_2\text{I}$  and  $\text{CCl}_2=\text{CClCH}_2\text{Br}$  with metallic mercury (in the absence of light in the case of the former, and in ultraviolet light in the case of the latter) led to the formation of completely stable  $\beta, \gamma$ -dichloroallyl mercuric iodide and  $\beta, \gamma, \gamma$ -trichloroallyl mercuric bromide:

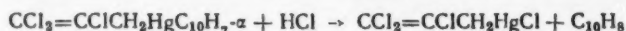


where X = H or Cl, and Y = Br or I. In the case of these compounds, the substitution reaction of the anion by the action of Ag<sub>2</sub>O (with subsequent neutralization with acid) occurs smoothly.

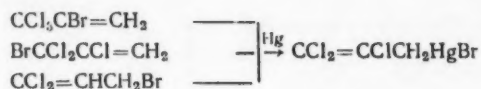
$\beta, \gamma, \gamma$ -Trichloroallyl mercuric bromide forms  $\beta, \gamma, \gamma$ -trichloroallyl- $\alpha$ -naphthyl mercury by reaction with  $\alpha$ -naphthyl magnesium bromide:



Under the action of HCl,  $\beta, \gamma, \gamma$ -trichloroallyl- $\alpha$ -naphthyl mercury decomposes as follows:



All the three isomeric trichlorobromopropenes give the same reaction product, viz.,  $\beta, \gamma, \gamma$ -trichloroallyl mercuric bromide upon reaction with mercury:



Obviously, in the first case, the reaction occurs with the homolytic isomerization of 1,1,1-trichloro-2-bromo-2-propene, and in the second case, with an allylic rearrangement. Not a single experiment with  $\text{BrCCl}_2\text{CCl}=\text{CH}_2$  allowed us to isolate the product of introduction of a mercury atom in a  $\text{BrCCl}_2$  group.

According to their reactivity with mercury, the three trichlorobromopropenes under investigation form the following sequence:  $\text{BrCCl}_2\text{CCl}=\text{CH}_2 > \text{CCl}_2=\text{CHCH}_2\text{Br} > \text{CCl}_3\text{CBr}=\text{CH}_2$ .

1,1,1-Trichloro-2-bromo-2-propene does not form organic mercury compounds with mercury in diffuse light, but in ultraviolet light it gives a 10-11% yield of  $\beta, \gamma, \gamma$ -trichloroallyl mercuric bromide. In diffuse light,  $\text{CCl}_2=\text{CClCH}_2\text{Br}$  forms  $\beta, \gamma, \gamma$ -trichloroallyl mercuric bromide in 2-3 days, and in ultraviolet light, in 3-4 hr. In the latter case, the yield is 34%. A mixture of  $\text{BrCCl}_2\text{CCl}=\text{CH}_2$  and  $\text{CCl}_3\text{CBr}=\text{CH}_2$  reacts with mercury with evolution of heat even in the absence of light, producing  $\beta, \gamma, \gamma$ -trichloroallyl mercuric bromide with a yield attaining 32%.

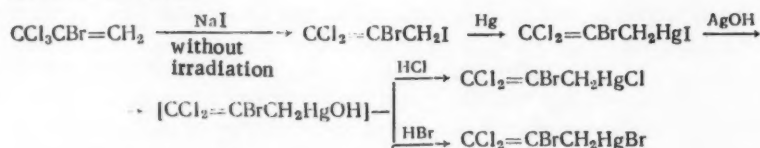
The increase of salt-like character in  $\beta$ -chloromercury allyl halides with increase in the number of halogen atoms in a molecule should be noted. Thus,  $\beta, \gamma, \gamma$ -trichloroallyl mercuric bromide does not give a symmetrical derivative under the action of ammonia, but forms an unstable complex  $\text{CCl}_2=\text{CClCH}_2\text{HgBr} \cdot \text{NH}_3$ . With sodium iodide, instead of giving a symmetrical compound, it exchanges the bromine atom of the bromomercury group for an iodine atom. Finally, under the action of sodium amalgam on  $\text{CCl}_2=\text{CClCH}_2\text{Br}$ , it is not bis- $\beta, \gamma, \gamma$ -trichloroallyl mercury which is formed, but  $\beta, \gamma, \gamma$ -trichloroallyl mercuric bromide:



In this respect, the trichloroallyl derivatives of mercury remind us of the trichloromethyl derivatives [9-11].

According to their thermal stability, the  $\beta, \gamma, \gamma$ -trichloroallyl mercuric halides synthesized from the following sequence:  $\text{CCl}_2=\text{CClCH}_2\text{HgCl} > \text{CCl}_2=\text{CClCH}_2\text{HgBr} > \text{CCl}_2=\text{CClCH}_2\text{HgI}$ .

The  $\beta$ -bromo- $\gamma, \gamma$ -dichloroallyl derivatives of mercury, synthesized along the same lines as the  $\beta, \gamma, \gamma$ -trichloroallyl mercuric halides were similar to the last named compounds from the point of view of thermal stability and characteristic chemical reactions.



For assaying the reactivity of chlorine atoms in the chloroallyl derivatives of mercury toward electrophilic reagents, we chose the reaction with silver nitrate. It appeared that at 20°  $\text{ClCH}=\text{CClCH}_2\text{HgI}$ ,  $\text{CCl}_2=\text{CClCH}_2\text{HgI}$ , and  $\text{CCl}_2=\text{CHCH}_2\text{HgI}$ \* lose only 1.5-2.2% of chlorine as AgCl in 48 hr, whereas  $\text{CH}_2=\text{CClCH}_2\text{HgI}$  is fully

\* For the synthesis and properties of these compounds, see [10, 11].

dehalogenated during the same period of time. Data characterizing the progress of this reaction at 49.7° are given in Table 1.

TABLE 1. Stability of  $\beta$ -Chloroallyl Mercuric Iodides Toward  $\text{AgNO}_3$  at 49.7°

| Mercuric iodide derivative              | Amount of lost chlorine by wt. % |      |       |
|---|----------------------------------|------|-------|
|   | 1 hr                             | 2 hr | 5 hr  |
| $\text{CH}_2=\text{CClCH}_2\text{HgI}$  | 100                              | —    | —     |
| $\text{CCl}_2=\text{CHCH}_2\text{HgI}$  | 55.4                             | 59.8 | 90.0  |
| $\text{CCl}_2=\text{CClCH}_2\text{HgI}$ | 0                                | 8.9  | 14.03 |
| $\text{ClCH}=\text{CClCH}_2\text{HgI}$  | 0                                | 0    | 12.75 |

These results indicate the considerable inactivity of chlorine in  $\beta, \gamma, \gamma$ -trichloroallyl and  $\beta, \gamma$ -dichloroallyl derivatives of mercury. Some of the data characterizing a series of compounds obtained in this work are gathered in Tables 2 and 3.

#### EXPERIMENTAL

**3-Iodo-2-bromo-1-propene.** A solution of 54.6 g (0.35 mole) of 3-chloro-2-bromo-1-propene and 55 g (0.37 mole) of sodium iodide in 150 ml of acetone was refluxed for 30 min; after cooling, the reaction mixture was diluted with 100 ml of hexane, and filtered. The solvent was driven off from the filtrate; the residue was

decolorized by shaking with powdered  $\text{Na}_2\text{S}_2\text{O}_3$ , filtered, and distilled twice under reduced pressure in a stream of nitrogen. Yield, 56.5 g (65% of the theoretical) of 3-iodo-2-bromo-1-propene, unstable in light, b. p. 54° (8 mm);  $n_D^{20}$  1.6130,  $d_4^{20}$  2.3608. Found: C 14.67, 14.92; H 1.75, 1.72%.  $\text{C}_3\text{H}_4\text{BrI}$ . Calculated: C 14.59; H 1.63%. The other halopropenes were synthesized in an analogous way (see Table 2).

**Reaction of 3-iodo-2-bromo-1-propene with mercury.** In a three-necked flask fitted with a hermetic seal and side-tube with trap, and dipped in an acetone bath at -60°, was placed 48 g (0.19 mole) of 3-iodo-2-bromo-1-propene. Metallic mercury (60 ml) was added with efficient stirring. The reaction started at once, and proceeded with heating and evolution of gas for 1.5 hr. A mobile liquid with a diene odor was collected in the trap. After evaporation in a measuring vessel, it occupied a volume of 4 liters (calculated for  $\text{CH}_2=\text{C}=\text{CH}_2$  at 20° and 760 mm, 4.6 liters). This substance did not give a precipitate with silver nitrate solution. Upon shaking with an equimolecular mixture of  $\text{HgCl}_2$  and  $\text{Hg}(\text{OCOCH}_3)_2$  in aqueous methanol, it formed a precipitate of  $\text{ClHgCH}_2\text{COCH}_2\text{HgCl}$  [13] characteristic for allene, it sublimed at 260-270°. Found: C 7.19, 7.23; H 0.82, 0.97%.  $\text{C}_3\text{H}_4\text{Cl}_2\text{Hg}_2\text{O}$ . Calculated: C 6.82; H 0.77%.

**$\beta, \gamma, \gamma$ -Trichloroallyl mercuric bromide.** A mixture of 10.2 g of  $\text{CCl}_2=\text{CClCH}_2\text{Br}$  and 250 g of metallic mercury was vigorously stirred for 2 hr in a quartz broad-necked test tube irradiated with a mercury lamp PRK-4 from a distance of 10 cm. Then the slurry was extracted with two portions of hot acetone. The acetone extract was evaporated in a stream of air at ordinary temperature. The residue of trichloroallyl mercuric bromide was washed with petroleum ether, and crystallized from chloroform. Yield, 6.6 g (34.2% of the theoretical). Under similar conditions,  $\beta, \gamma, \gamma$ -trichloroallyl mercuric bromide was prepared from  $\text{CCl}_3\text{CBr}=\text{CH}_2$  and a mixture\* of  $\text{BrCCl}_2\text{CCl}=\text{CH}_2$  and  $\text{CCl}_3\text{CBr}=\text{CH}_2$  containing 60% of  $\text{BrCCl}_2\text{CCl}=\text{CH}_2$  (see Table 3).

When ammonia is passed through a chloroform solution of  $\beta, \gamma, \gamma$ -trichloroallyl mercuric bromide, glistening platelets of the complex  $\text{CCl}_2=\text{CClCH}_2\text{HgBr} \cdot \text{NH}_3$  separate out. Yield, quantitative. Upon boiling for 5 min with acetone, the complex decomposes completely to  $\text{CCl}_2=\text{CClCH}_2\text{HgBr}$  and  $\text{NH}_3$  (see Table 3).

**$\beta, \gamma, \gamma$ -Trichloroallyl mercuric chloride.** A solution of 0.8 g of  $\beta, \gamma, \gamma$ -trichloroallyl mercuric bromide in 20 ml of alcohol was refluxed for 15 min with silver oxide (from 0.5 g of  $\text{AgNO}_3$ ). The precipitate produced was filtered off, and the filtrate poured into water. The turbid solution thus obtained was clarified by centrifugation, and then treated with 5% hydrochloric acid until acid to litmus. The precipitate of  $\beta, \gamma, \gamma$ -trichloroallyl mercuric chloride, which separated out, was filtered off, and recrystallized from acetone by cooling to -30° a solution which was obtained at about 20°. The following compounds:  $\text{CCl}_2=\text{CBrCH}_2\text{HgCl}$ ,  $\text{CHCl}=\text{CClCH}_2\text{HgBr}$  and  $\text{CCl}_2=\text{CBrCH}_2\text{HgBr}$  were synthesized in a similar way (see Table 3; the last two compounds with the use of  $\text{HBr}$  instead of  $\text{HCl}$ ).

**$\beta, \gamma, \gamma$ -Trichloroallyl- $\alpha$ -naphthyl mercury.** A solution of 6.3 g of  $\beta, \gamma, \gamma$ -trichloroallyl mercuric bromide in 100 ml of ether was treated during 30 min with 25 ml of a solution of  $\alpha\text{-C}_{10}\text{H}_7\text{MgBr}$  prepared from 2.4 g of  $\text{Mg}$ , 20.7 g of  $\alpha\text{-C}_{10}\text{H}_7\text{Br}$ , and 100 ml of ether. After refluxing for 1 hr, the mixture was poured into water. The emulsion thus obtained was extracted with ether. After evaporation of the ether, the residue was chromatographed on  $\text{Al}_2\text{O}_3$  (benzene was used for elution). Yield of  $\beta, \gamma, \gamma$ -trichloroallyl- $\alpha$ -naphthyl mercury, 2.4 g (34.4% of the theoretical) (see Table 3).

\* Obtained as described in [14], with irradiation with ultraviolet light. The composition was determined by distillation of the diethylamine derivatives of the components [14].

**$\beta, \gamma, \gamma$ -Trichloroallyl mercuric iodide.** A mixture of 4.3 g of  $\text{CCl}_2=\text{CClCH}_2\text{I}$  and 221 g of metallic mercury was left to stand for 12 hr with periodic shaking. The reaction mixture was extracted with hot acetone. After centrifugation, evaporation of the solvent, and recrystallization of the residue from alcohol, 1.8 g (2.4% of the theoretical) of  $\beta, \gamma, \gamma$ -trichloroallyl mercuric iodide was obtained. The following:  $\text{CH}_2=\text{CClCH}_2\text{HgI}$ ,  $\text{CHCl}=\text{CClCH}_2\text{HgI}$  and  $\text{CCl}_2=\text{CBrCH}_2\text{HgI}$  were synthesized in an analogous way (see Table 3).

TABLE 2. Starting Halopropenes

| Formula                                   | B. p. °C.<br>(mm Hg) | $n_D^{20}$ | $d_4^{20}$ | Found %        |              | Calculated % |      |
|---|----------------------|------------|------------|----------------|--------------|--------------|------|
|   |                      |            |            | C              | H            | C            | H    |
| $\text{CH}_2=\text{CClCH}_2\text{I}$      | 45(15)               | 1,5760     | —          | 18,39<br>18,43 | 2,13<br>2,14 | 17,81        | 2,00 |
| $\text{CH}_2=\text{CBrCH}_2\text{Br}^*$   | 58(35)               | 1,5430     | 2,0511     | 18,22<br>18,11 | 2,19<br>2,02 | 18,03        | 2,02 |
| $\text{CHCl}=\text{CClCH}_2\text{I}$      | 64(7)                | 1,6118     | —          | 15,19<br>15,20 | 1,24<br>1,36 | 15,21        | 1,28 |
| $\text{CCl}_2\text{CClCH}_2\text{I}^{**}$ | 56(4)                | 1,6100     | 2,1435     | 13,38<br>13,36 | 0,77<br>0,74 | 13,27        | 0,74 |
| $\text{CCl}_2=\text{CBrCH}_2\text{I}$     | 82—84(4)             | 1,6382     | —          | 11,50<br>11,67 | 0,56<br>0,68 | 11,41        | 0,64 |

\* Picrate of isothiuronon salt (prepared as described in [12]:  $\text{CH}_2=\text{CBrCH}_2\text{SC}(=\text{NH})\text{NH}_2 \cdot \text{C}_6\text{H}_5(\text{NO}_2)_3\text{OH}$ ; b. p. 169–169,5°. Found: C 28,37, 28,41; H 2,26, 2,40; N 16,62, 16,53%. Calculated: C 28,32; H 2,38; N 16,51%.

\*\* Picrate of isothiuronon salt:  $\text{CCl}_2=\text{CClCH}_2\text{SC}(=\text{NH})\text{NH}_2 \cdot \text{C}_6\text{H}_5(\text{NO}_2)_3\text{OH}$ ; b. p. 175–176° (dec.). Literature data [12]: b. p. 175–176°. Found: N 15,80, 15,92%. Calculated: N 15,61%.

TABLE 3. Mercury Organic Compounds Synthesized

| Formula  | Yield<br>(% of<br>theoretical) | M. p.,<br>°C   | Found %        |              |                |                | Calculated % |      |       |       |
|--|--------------------------------|----------------|----------------|--------------|----------------|----------------|--------------|------|-------|-------|
|  |                                |                | C              | H            | Hal            | Hg             | C            | H    | Hal   | Hg    |
| $\text{CH}_2=\text{CClCH}_2\text{HgI}$                       | 36,4                           | 94–95<br>***   | 8,87<br>8,65   | 1,10<br>1,09 | 40,54<br>40,61 | 49,32<br>49,59 | 8,94         | 1,00 | 40,29 | 49,78 |
| $\text{CHCl}=\text{CClCH}_2\text{HgI}$                       | 45                             | 83–86<br>***   | 8,71<br>8,70   | 1,08<br>1,02 | 44,51<br>44,67 | 45,20<br>45,09 | 8,24         | 0,69 | 45,21 | 45,85 |
| $\text{CHCl}=\text{CClCH}_2\text{HgBr}$                      | 34,5                           | 78<br>***      | 9,24<br>9,32   | 0,85<br>1,69 | 38,72<br>33,68 | 50,73<br>50,93 | 9,23         | 0,76 | 38,62 | 51,37 |
| $\text{CCl}_2=\text{CClCH}_2\text{HgBr}^*$                   | 34,2                           | 123–<br>123,5  | 8,33<br>8,44   | 0,48<br>1,69 | 43,53<br>43,74 | —              | 8,48         | 0,47 | 43,83 | —     |
| $\text{CCl}_2=\text{CClCH}_2\text{HgCl}$                     | 28                             | 157,5<br>***   | 9,50<br>9,21   | 0,48<br>0,51 | —              | —              | 9,47         | 0,53 | —     | —     |
| $\text{CCl}_2=\text{CClCH}_2\text{HgI}$                      | 24                             | 124–<br>125,5  | 7,63<br>7,51   | 0,49<br>0,27 | 49,09<br>49,38 | 42,33<br>42,26 | 7,63         | 0,93 | 49,43 | 42,51 |
| $\text{CCl}_2=\text{CBrCH}_2\text{HgI}$                      | 31                             | 115–116<br>*** | 7,02<br>6,91   | 0,40<br>0,46 | 53,36<br>53,22 | 39,17<br>39,03 | 6,97         | 0,39 | 53,79 | 38,85 |
| $\text{CCl}_2=\text{CBrCH}_2\text{HgCl}$                     | 44,5                           | 164–166<br>*** | 8,52<br>8,53   | 0,39<br>0,43 | 43,33<br>—     | 46,95<br>47,60 | 8,48         | 0,47 | 43,83 | 47,20 |
| $\text{CCl}_2=\text{CClCH}_2\text{HgC}_{10}\text{H}_7\alpha$ | 34,4                           | 128–<br>129,5  | 32,87<br>32,97 | 1,91<br>2,01 | 22,84<br>23,06 | 41,90<br>42,16 | 33,07        | 1,92 | 22,53 | 42,48 |
| $\text{CCl}_2=\text{CClCH}_2\text{HgBrNH}_2^{**}$            | 100                            | 128–130<br>*** | 8,32<br>8,30   | 0,93<br>0,81 | —              | —              | 8,15         | 1,14 | —     | —     |

\* From  $\text{CCl}_2=\text{CClCH}_2\text{Br}$ .

\*\* Found: N 3,04, 2,86%. Calculated: N 3,17%.

\*\*\* With decomposition.

**Reaction of  $\beta, \gamma, \gamma$ -trichloroallyl mercuric bromide with sodium iodide.** A solution of 0.4 g of  $\text{CCl}_2=\text{CClCH}_2\text{HgBr}$  in acetone and a solution of 0.5 g of NaI in the same solvent were mixed together. The precipitate, which separated out, was filtered off. The filtrate was poured on water, and the precipitate of  $\beta, \gamma, \gamma$ -trichloroallyl mercuric iodide

thus formed was filtered off, and recrystallized, first from a 1:1 mixture of acetone and methanol, and then from chloroform. Yield, 0.2 g (45% of the theoretical) m. p., and mixed m. p. with an authentic sample of this substance, both 124-125°.

Reaction of 1,1,2-trichloro-3-bromo-1-propene with sodium amalgam. Cooled sodium amalgam (prepared from 0.5 g of Na and 20 ml of mercury) was treated with 0.5 ml of methyl acetate, and, while stirring vigorously, with 8 ml of 1,1,3-trichloro-2-bromo-1-propene added in 3 portions. The mixture was protected from air and light, and left to stand for 5 days. Then it was treated with 20 ml of boiling acetone. The part of the reaction mixture containing mercury was centrifuged. The cherry-red liquid thus obtained was evaporated to  $\frac{1}{4}$  of its volume, and the precipitate formed was filtered off, washed with hexane, and recrystallized (from a mixture of alcohol and chloroform) to give 4.7 g (31% of the theoretical) of  $\beta, \gamma, \gamma$ -trichloroallyl mercuric bromide, m. p. 119-121°. Found: C 8.73, 8.76; H 0.47, 0.66; halogen 43.44, 43.67; Hg 47.10, 47.07%.  $C_3H_2Cl_3BrHg$ . Calculated: C 8.48; H 0.47; halogen 43.83; Hg 47.20%.

Reaction of  $\beta$ -chloroallyl mercuric iodide with  $\alpha$ -naphthyl magnesium bromide. A Grignard reagent prepared from 2.4 g of magnesium and 20.7 g of  $\alpha$ -bromonaphthalene (in 50 ml of tetrahydrofuran) was treated dropwise with a solution of 20 g of  $\beta$ -chloroallyl mercuric iodide in 50 ml of tetrahydrofuran. After refluxing for 1 hr (allene was produced, tested with  $HgCl_2$  solution), the reaction product was cooled, decomposed with water, and extracted with ether. The aqueous part of this product gave 8 g of metallic mercury (80% of the amount used). The ethereal layer was separated, dried over calcium chloride, and evaporated to dryness. The residue thus obtained was recrystallized twice from a 1:1 mixture of tetrahydrofuran and acetone. Yield, 2 g of  $\alpha$ -naphthyl mercuric iodide, m. p. 185°; reported m. p. [15], 185°. Found: C 26.87, 26.69; H 1.60, 1.61; I 28.36, 28.32%.  $C_{10}H_7HgI$ . Calculated: C 26.42; H 1.55; I 27.93%.

Action of silver nitrate on haloallyl derivatives of mercury. A weighted amount of the organic mercury compound of the type  $CX_2=CHCH_2HgI$ , where X was H or Cl, was dissolved in 2 ml of acetone. After addition of 10 ml of alcohol, this solution was treated with 20 ml of 0.1 N alcoholic  $AgNO_3$ . The reaction mixture was kept in a thermostat at  $49.7 \pm 0.1^\circ$  for 1, 2, and 5 hr. The precipitate of silver halide was filtered off, and washed with methanol and ether. After drying for 0.5 hr in a current of air in a dark place, the silver halide was weighed. In a separate experiment, it was determined that under the given conditions, all the iodine present in the organic mercury compound was precipitated as  $AgI$ . The yield of  $AgCl$  was obtained by subtracting the calculated weight of  $AgI$  from the total weight of the silver halide.

#### SUMMARY

1.  $\beta$ -Haloallyl derivatives of mercury with the general structure  $CX_2=CHCH_2HgZ$ , where X = H or Cl, or Br, and Z is a halogen atom or an  $\alpha$ - $C_{10}H_7$  radical were synthesized.
2. The thermal stability of the compounds synthesized increased with the number of halogen atoms in the molecule.

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# THE CONDENSATION PRODUCTIONS OF CHLORAL AND THE AMIDES OF ORGANOPHOSPHORIC ACIDS

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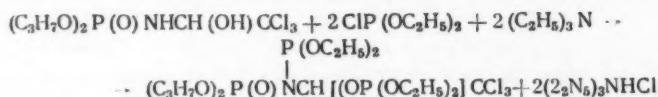
Original article submitted August 28, 1959

Recently the attention of investigators has been turned to synthetic products formed by the reaction of chloral with dialkyl- and trialkylphosphites, since many of these compounds possess insecticidal properties. It was therefore of interest to obtain the condensation products of chloral with the amides of organophosphoric acids. In this paper we present the results of studies of the reaction of chloral with some amides of dialkylphosphoric acids.

Our experiments showed that this reaction leads to the formation of N- $\alpha$ -hydroxy- $\beta$ -trichloroethylamides of dialkylphosphoric acids according to the following scheme



In order to confirm the structure of the compounds described, one of them ( $R = C_3H_7$ ) was reacted with the chloroanhydride of diethylphosphoric acid. In the case of the structure indicated, the hydrogens of the amide and hydroxyl groups must be replaced in the organophosphoric residues.



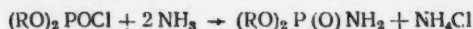
As indicated, the exchange reaction takes place easily and completely in an ether solution. The reaction of chloral with the amides of dialkylphosphoric acids takes place on heating equimolecular quantities of the reagents for from one to one and a half hours at a temperature of 60-90°. In this way we obtained quantitative yields of N- $\alpha$ -hydroxy- $\beta$ -trichloroethylamides of dialkylphosphoric acids  $(RO)_2P(O)NHCH(OH)CCl_3$ , where the alkyl groups were methyl, ethyl, propyl, isopropyl, and butyl. The formulas of the compounds, their melting points and analytical data are shown in the following table.

| Compound No. | Formula                          | M. p., °C             | Phosphorus content, % |            |
|--------------|----------------------------------|-----------------------|-----------------------|------------|
|              |                                  |                       | found                 | calculated |
| I            | $(CH_3O)_2P(O)NHCH(OH)CCl_3$     | 103-104               | 11,78; 11,70          | 11,38      |
| II           | $(C_2H_5O)_2P(O)NHCH(OH)CCl_3$   | 96-97                 | 10,38; 10,49          | 10,32      |
| III          | $(C_3H_7O)_2P(O)NHCH(OH)CCl_3$   | 81-82                 | 9,47; 9,45            | 9,44       |
| IV           | $(i-C_3H_7O)_2P(O)NHCH(OH)CCl_3$ | 138-139               | 9,43; 9,64            | 9,44       |
| V            | $(C_4H_9O)_2P(O)NHCH(OH)CCl_3$   | 79-80                 | 8,7; 8,77             | 8,69       |
| VI           | $C_2H_5OP(O)[NHCH(OH)CCl_3]_2$   | Thick, viscous liquid |                       |            |
| VII          | $(C_2H_5)_2P(O)NHCH(OH)CCl_3$    | Thick liquid          |                       |            |

Most of the substances shown in the table are crystalline and are soluble in the ordinary organic solvents. The substances that have one of the lower hydrocarbon radicals adjacent to the phosphorus are also soluble in water. The melting points of the crystalline products did not show the regularity which is usually observed in compounds of a homologous series. For example, N- $\alpha$ -hydroxy- $\beta$ -trichloroethylamide of diisopropylphosphoric acid (IV) melts considerably higher than the corresponding compound, which has a complex hydrocarbon chain in the ester group next to the phosphorus (III). Similar departures from normal occur in connection with other compounds. Preliminary study of the insecticidal properties of compounds (I) and (II) showed that their aqueous solutions caused the death of house flies.

## EXPERIMENTAL

Unsubstituted amides of organophosphoric acids were obtained by the action of dry gaseous ammonia on ether solutions of alkylchlorophosphates.



The ammonium chloride precipitate was filtered off and the amide, after removal of the solvent, was condensed with chloral. In those cases where the amides obtained were not soluble in ether and separated out with the ammonium chloride, the mixture was not separated but was used for the subsequent reaction. The quantity of amide was calculated in accordance with the theoretical composition of the mixture. Such mixtures of an amide with ammonium chloride were formed in the production of the amide of dimethylphosphoric acid and the diamide of ethylphosphoric acid.

N- $\alpha$ -hydroxy- $\beta$ -trichloroethylamide of dimethylphosphoric acid (I). For the reaction the amide of dimethylphosphoric acid  $(CH_3O)_2P(O)NH_2$  mixed with ammonium chloride was used (see the preparation of the amides of organophosphoric acids). The theoretical content of amide in the mixture was 70%. For the reaction 6.26 g of a mixture containing 4.38 g (0.035 M) of the amide  $(CH_3O)_2P(O)NH_2$  and 5.16 g (0.035 M) of chloral were used. The reaction mixture was stirred and heated on a water bath at a temperature of 90-95° for one and a half hours. After cooling, the thick mass was dissolved in 10 ml of ether. The precipitate of ammonium chloride was filtered off. After removing the solvent from the filtrate, 7.9 g (82.9%) of a thick liquid was obtained. On the following day the reaction product became a dense, white mass of crystals. The substance on recrystallization from petroleum ether (b. p. 70-120°) formed small needles with a m. p. 103-104°. Found: P 11.78, 11.70%.  $C_4H_9O_4PNC l_3$ . Calculated: P 11.38%. The substance dissolves easily in water, benzene and dioxane (on heating), is relatively insoluble in ether, and is almost completely insoluble in boiling petroleum ether.

N- $\alpha$ -hydroxy- $\beta$ -trichloroethylamide of diethylphosphoric acid (II). To a suspension of 5.4 g (0.035 M) of the amide of diethylphosphoric acid  $(C_2H_5O)_2P(O)NH_2$  in ether 5.16 g (0.035 M) of chloral was added immediately. The temperature rose from 21 to 36°. The reaction mixture was stirred and heated on a water bath at 90-100° for 2 hr. On the following day the mass crystallized. After recrystallization from petroleum ether small needles with a melting point of 96-97° were obtained. Found: P 10.38, 10.49%.  $C_6H_{13}O_4PNC l_3$ . Calculated: P 10.32%. The substance is soluble in ether, benzene, dioxane, petroleum ether (on heating), and also in water.

N- $\alpha$ -hydroxy- $\beta$ -trichloroethylamide of dipropylphosphoric acid (III). In order to produce the N-monosubstituted amide, 6.34 g (0.035 M) of the amide of dipropylphosphoric acid  $(C_3H_7O)_2P(O)NH_2$  was allowed to react with 5.16 g (0.035 M) of chloral. After the addition of the chloral to the amide, the temperature of the mixture decreased from 21 to 16°. The reaction mixture was stirred and heated on a water bath at 90-96° for one hour. On cooling, the contents of the flask became a dense, white, crystalline mass. The product was crystallized from petroleum ether and yielded fine, white needles with a melting point of 81-82°. Found: P 9.47, 9.45%.  $C_8H_{17}O_4PNC l_3$ . Calculated: P 9.44%. The substance is soluble in ether, alcohol, and water (after prolonged contact), and it is soluble in petroleum ether on heating.

N- $\alpha$ -hydroxy- $\beta$ -trichloroethylamide of diisopropylphosphoric acid (IV). The N-monosubstituted amide of diisopropylphosphoric acid was obtained in a similar manner by the action of chloral (0.035 M) on the amide of diisopropylphosphoric acid  $(i-C_3H_7O)_2P(O)NH_2$  (0.035 M). Within 50 min after heating the mixture (bath temperature 90-96°), the reaction product crystallized completely while still hot. The N-monosubstituted amide, after recrystallization from a mixture of benzene and petroleum ether (1:1; b. p. petroleum ether 70-120°), formed small needles, m. p. 138-139°. The yield of pure product was 7.3 g (63.5%). Found: P 9.43, 9.64%.  $C_8H_{17}O_4PNC l_3$ . Calculated: P 9.44%. The substance is soluble in ether, in benzene on heating, and almost completely insoluble in hot petroleum ether.

N- $\alpha$ -hydroxy- $\beta$ -trichloroethylamide of dibutylphosphoric acid (V). The N-monosubstituted amide of dibutylphosphoric acid was obtained in a similar manner to the preceding substituted amides. The product was recrystallized from petroleum ether (b. p. 70-120°). On drying, the substance does not crumble but forms a dense mass which must be cut and crushed with a spatula; m. p. 79-80°. Found: P 8.7, 8.77%.  $C_{10}H_{21}O_4PNC l_3$ . Calculated: P 8.69%. The substance dissolves easily in ether, and in petroleum ether on heating; it is insoluble in water.

Di-N- $\alpha$ -hydroxy- $\beta$ -trichloroethylamide of ethylphosphoric acid (VI). The diamide of ethylphosphoric acid  $(C_2H_5O)_2P(O)(NH_2)_2$  in a mixture of ammonium chloride (see the production of the amides of organophosphoric acids)

with a theoretical content of 53.7% of the diamide was used for the reaction. To a suspension of 6.14 g of the mixture of diamide and ammonium chloride containing 3.3 g (0.0266 M) of the diamide in ether was added 7.83 g (0.0532 M) of chloral. Since the diamide is hygroscopic, measures were taken to prevent moisture from the air from entering the reaction vessel. The reaction mixture was heated with stirring on a water bath at 50-60° for one and a half hours. After cooling, the reaction product was dissolved in ether and the ammonium chloride filtered off. After removing the solvent 11 g (98.7%) of a very thick, viscous liquid was obtained which did not crystallize even after prolonged standing. The substance was not soluble in ether, benzene or water.

N- $\alpha$ -hydroxy- $\beta$ -trichloroethylamide of diethylphosphoric acid (VII). 4.35 g (0.036 M) of the amide of diethylphosphoric acid  $(C_2H_5)_2P(O, NH_2)$  was allowed to react with 5.3 g (0.036 M) of chloral. On mixing these substances together the temperature of the mixture, despite cooling of the flask by a stream of water, rose from 21 to 65°. The reaction mixture was stirred and heated for 1 hr on a water bath at a temperature of 60-65°. The product obtained was a very thick liquid which did not crystallize even after prolonged standing. The substance was only slightly soluble in ether, benzene (with heating), and water.

The action of the chloroanhydride of diethylphosphoric acid on N- $\alpha$ -hydroxy- $\beta$ -trichloroethylamide of diisopropylphosphoric acid. To a solution of 3.94 g (0.12 M) of the amide  $(C_3H_7O)_2P(O)NHCH(OH)CCl_3$  (m. p. 81-82°) in 60 ml of ether was added 3.75 g (0.024 M) of an ether solution of diethylchlorophosphite  $(C_2H_5O)_2PCl$  (b. p. 72-73° [60 mm]) through a dropping funnel, with stirring, in a flask cooled by water. After the addition of the chloride the thick mass was stirred for 2 hr while the solvent was allowed to boil lightly. 3.22 g (97.1%) of the salt of the amide  $(C_2H_5)_3N \cdot HCl$  and a residue of 6.43 g (94.3%) after removal of the solvent were obtained.

The reaction product was a fairly mobile liquid with an ether-like odor. On distillation in vacuo (1 mm), the substance decomposed (bath temperature 175-200°).

#### SUMMARY

A number of monosubstituted amides  $(RO)_2P(O)NHCH(OH)CCl_3$  were obtained by the reaction of chloral with dialkylphosphoric acids, and subsequently characterized.

## PART 22. ADDITION OF PHOSPHORUS PENTACHLORIDE TO ISOPROPENYLACETYLENE

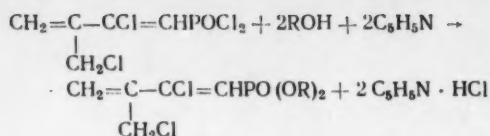
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It has been established [4-5] that phosphorus pentachloride in the crystalline state has the structure of the complex  $[\text{PCl}_4]^+ \cdot [\text{PCl}_6]^-$ . We carried out the reaction in a benzene solution, i.e., in a solvent in which phosphorus pentachloride is soluble to only a slight extent, so that one may assume that the reaction proceeded heterolytically. It would therefore be more accurate to formulate the addition product as a complex of the structure  $\text{RCHCl}-\text{CH}_2\text{P}^+\text{Cl}_5 \cdot \text{P}^-\text{Cl}_6$ , especially in view of the fact that complexes which contain cations of this type have already been described [6-7]:  $\text{RPCl}_3^+, \text{FeCl}_4^-, \text{RPCl}_3^+ \cdot \text{Al}^-\text{Cl}_4$ .

$$\begin{array}{c}
 \text{CH}_2=\text{C}-\text{C}\equiv\text{CH} + 2\text{PCl}_5 \begin{cases} \nearrow \text{CH}_2\text{Cl}-\text{CCl}-\text{CCl}=\text{CHCl} \\ \searrow \text{CH}_2=\text{C}-\text{CCl}=\text{CHPCl}_3 \cdot \text{PCl}_5 \end{cases} \xrightarrow{\text{SO}_2} \\
 \quad \quad \quad | \\
 \quad \quad \quad \text{CH}_3 \\
 \text{CH}_2\text{Cl}-\text{CCl}-\text{CCl}=\text{CHCl} \\
 \quad \quad \quad | \\
 \quad \quad \quad \text{CH}_3 \\
 \rightarrow \text{CH}_3=\text{C}-\text{CCl}=\text{CHPOCl}_2 + \text{POCl}_3 + 2\text{SOCl}_2 + \text{HCl} \\
 \quad \quad \quad | \\
 \quad \quad \quad \text{CH}_2\text{Cl}
 \end{array}$$

1,2,3,4-Tetrachloro-3-methylbutene-1 is a colorless liquid which dissolves in all organic solvents and decolorizes bromine water. Investigation of the properties of the chloride of (2-chloromethyl-3-chlorobutadiene-1,3)-4-phosphinic acid showed that it reacts readily with alcohols. This made it possible to prepare neutral esters of the acid by applying the reaction described by Milobendzki and Sachnovski [8]:

55



By employing this reaction, the dimethyl, diethyl, and di-n-propyl esters of (2-chloromethyl-3-chlorobutadiene-1,3)-4-phosphinic acid were prepared. Their physical constants are listed in Table 2.

TABLE 1

| Formula   | B.p., °C<br>(pressure<br>in mm<br>Hg) | $n_D^{20}$ | $d_4^{20}$ | Yield,<br>% | MR    |            |
|---|---------------------------------------|------------|------------|-------------|-------|------------|
|   |                                       |            |            |             | found | calculated |
| $\text{CH}_2\text{Cl}-\text{CCl}-\text{CHCl}-\text{CHCl}$   | 60 (3)                                | 1,5192     | 1,4304     | 16,7        | 44,22 | 44,29      |
| $\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_2-\text{C}-\text{CCl}-\text{CHPOCl}_2 \\   \\ \text{CH}_2\text{Cl} \end{array}$ | 121 (3)                               | 1,5405     | 1,5400     | 59          | 51,75 | 52,14      |

TABLE 2

| Formula   | B.p., °C<br>(pressure<br>in mm<br>Hg) | $n_D^{20}$ | $d_4^{20}$ | Yield,<br>% | MR    |            |
|---|---------------------------------------|------------|------------|-------------|-------|------------|
|   |                                       |            |            |             | found | calculated |
| $\text{CH}_2-\text{C}-\text{CCl}-\text{CHPO}(\text{OCH}_3)_2$   | 136 (3)                               | 1,4957     | 1,3155     | 69          | 54,36 | 54,17      |
| $\begin{array}{c} \text{CH}_2\text{Cl} \\   \\ \text{CH}_2-\text{C}-\text{CCl}-\text{CHPO}(\text{OC}_2\text{H}_5)_2 \\   \\ \text{CH}_2\text{Cl} \end{array}$ | 142,5 (2)                             | 1,4838     | 1,2365     | 73          | 63,15 | 63,41      |
| $\begin{array}{c} \text{CH}_2\text{Cl} \\   \\ \text{CH}_2-\text{C}-\text{CCl}-\text{CHPO}(\text{OC}_4\text{H}_9)_2 \\   \\ \text{CH}_2\text{Cl} \end{array}$ | 158 (2)                               | 1,4805     | 1,1749     | 67          | 72,78 | 72,66      |

The esters of (2-chloromethyl-3-chlorobutadiene-1,3)-4-phosphinic acid are colorless, mobile liquids which give a positive reaction for chlorine, decolorize bromine water, and dissolve in ordinary organic solvents. They polymerize readily when stored.

To establish the structure of the reaction products, we used infrared spectroscopy. The infrared spectra of the compounds were determined on a D-209 Hilger spectrometer with a sodium chloride prism in the 700-2000  $\text{cm}^{-1}$  range and an IKS-1 spectrometer with a lithium fluoride prism in the 2500-3600  $\text{cm}^{-1}$  range. Analysis of the infrared spectrum of the first reaction product indicated that the constitution of the compound which had been synthesized most likely corresponded to the formula  $\text{CHCl}=\text{CCl}-\text{CCl}-\text{CH}_2\text{Cl}$ .



and the chemical properties of the compound confirmed this. In spectra of compounds of the type  $\text{CH}_2=\text{CH}-$  or  $\text{CH}_2=\text{C}-$  the absorption bands of the double bond  $\text{C}=\text{C}$  are situated in the 1640-1650  $\text{cm}^{-1}$  region [9], whereas in the spectrum of the tetrachloromethylbutene prepared by us the band in question is in the vicinity of 1612  $\text{cm}^{-1}$  (Fig. 1). Lowering the frequency of the vibration of the double bond in nonchlorinated olefins takes place because of the influence of the adjacent chlorine atoms; the same lowering of the double bond frequency is observed in spectra of other compounds which have chlorine atoms next to the double bond [10, 11].

In the compound investigated by us the chlorine atoms at the double bond are in a cis-configuration. This follows from a comparison of the spectrum of this compound with the spectrum of 1,2-dichloro-1-propene  $\text{CCl}=\text{CHCl}$ :



[4]. Just like the spectrum of the cis-isomer of dichloropropene, the spectrum of the tetrachloromethylbutene has strong absorption bands at 1612 and 1010  $\text{cm}^{-1}$ , whereas the spectrum of the trans-isomer of dichloropropene has an absorption band of low intensity in the region of 1612  $\text{cm}^{-1}$ , and instead of the strong band at 1010  $\text{cm}^{-1}$ , which is characteristic for the cis-isomer, shows a strong absorption band at 950-990  $\text{cm}^{-1}$ .

Chlorine atoms exert a strong influence on the CH bonds adjacent to them. According to data reported by Bennett and Meyer [12], the frequency of the antisymmetric valency vibration of the CH bond in methyl chloride is raised by  $80\text{ cm}^{-1}$  due to the effect of the adjacent chlorine atom, while the frequency of the symmetric vibration is raised by  $94\text{ cm}^{-1}$ . One band of the valency vibration of the CH bond (at  $3019\text{ cm}^{-1}$ ) corresponds to the  $\approx\text{CH}$  group in the spectra of olefins [13], whereas in the spectra of saturated hydrocarbons two bands (one of the antisymmetric valency vibration of the CH bond at  $2926\text{ cm}^{-1}$  and one of the symmetric vibration at  $2853\text{ cm}^{-1}$ ) correspond to the  $>\text{CH}_2$  group. If it is assumed that chlorine atoms increase the frequency of valency vibrations of CH

bonds in compounds of the types  $\text{R}-\text{C}=\text{C}\begin{smallmatrix} \text{Cl} \\ \text{H} \end{smallmatrix}$  and  $\text{CH}_2\text{Cl}$  by the same values of  $80$  and  $94\text{ cm}^{-1}$  as in methyl chloride, one may ascribe the absorption band at  $3103\text{ cm}^{-1}$  ( $3019 + 80\text{ cm}^{-1}$ ) in the spectrum of the compound investi-

gated by us to valency vibrations of the CH bond in the  $=\text{C}\begin{smallmatrix} \text{Cl} \\ \text{H} \end{smallmatrix}$  group, and the absorption bands at  $3000\text{ cm}^{-1}$  ( $2926 + 80\text{ cm}^{-1}$ ) and  $2945\text{ cm}^{-1}$  ( $2853 + 94\text{ cm}^{-1}$ ) to the antisymmetric and symmetric vibrations of the methylene groups at the fourth carbon atom. The discrepancy between the position of the bands observed in the spectrum and their position calculated by adding the appropriate correction to the characteristic CH frequency (cf. figures in parentheses) amounts to only a few inverse centimeters; this is within the limits of experimental error in the measurements and indicates that our conclusions are justified.

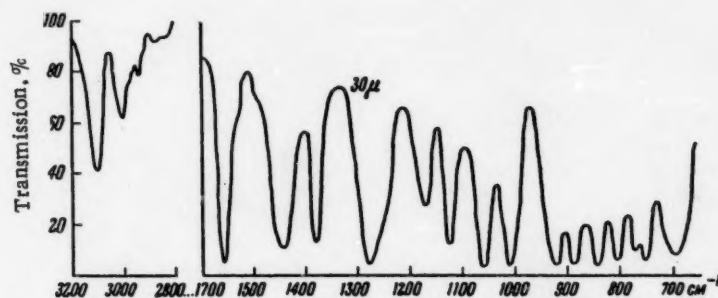


Fig. 1. Infrared spectrum of 1,2,3,4-tetrachloro-3-methylbutene-1.

The presence of a  $\text{CH}_3$  group in the molecule of the compound synthesized by us was indicated by the two weak absorption bands at  $2961$  and  $2881\text{ cm}^{-1}$  in its spectrum. These bands, as demonstrated by Fox and Martou [13], correspond to the antisymmetric and symmetric vibrations of the CH bonds in the  $\text{CH}_3$  group. As can be seen from the spectrum, the intensities of the  $3103$ ,  $3000$ , and  $2945\text{ cm}^{-1}$  bands are much greater than those of the  $2961$  and  $2881\text{ cm}^{-1}$  bands; it follows from this that the effect of the adjacent chlorine atoms increases the polarity of the CH bonds and, consequently, also the intensity of the corresponding bands in the spectrum.

The infrared spectrum of the second reaction product (Fig. 2) gave reasons to assume that the structure of the product corresponded to that of the chloride of (2-chloromethyl-3-chlorobutadiene-1,3)-4-phosphinic acid  $\text{CH}_2=\text{C}-\text{CCl}=\text{CHPOCl}_2$ . The presence of a vinylidene group at the end of the molecule followed from the fact



that an  $882\text{ cm}^{-1}$  band, which is characteristic for this group, was observed in the spectrum. The spectrum of this compound also indicated conjugation of  $\text{C}=\text{C}$  bonds.

It is known that when conjugation occurs there is splitting of the  $\text{C}=\text{C}$  absorption band into two bands [14, 15] and displacement of these bands towards lower frequencies [16]. The bands corresponding to conjugated bonds in our compound had the frequencies of  $1645$  and  $1587\text{ cm}^{-1}$ . To determine the degree of conjugation of the double bonds, we investigated the Raman spectrum of this compound and measured the intensity of the  $1645\text{ cm}^{-1}$  band which corresponds to vibrations of the double bond:

( $\nu$ ,  $\text{cm}^{-1}$ ): 298 (2), 357 (2), 412 (1), 476 (1), 514 (2), 532 (1), 569 (3), 594 (2), 664 (4), 98 (9 broad), 799 (1),

840 (3), 883 (1), 921 (2), 1038 (3), 1106 (1), 1178 (3), 1233 (4), 1280 (7 broad), 1388 (3), 1411 (3), 1470 (4), 1645 (10), 2853 (3), 2925 (6), 2962 (7).

In the Raman spectrum of pentene-1 ( $\text{CH}_3-\text{CH}_2\text{CH}_2-\text{CH}=\text{CH}_2$ ) the band corresponding to vibration of the double bond has an intensity of 30 units, while in the spectrum of butadiene ( $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$ ) the intensity of this band increases tenfold because of conjugation, i.e., it is equal to 300 units. In the case of 2-methyl-1,3-butadiene the intensity of the band of double bond vibration is only six times greater than that of the pentene-1 band, because conjugation is interfered with to some extent by reason of steric hindrance [17].

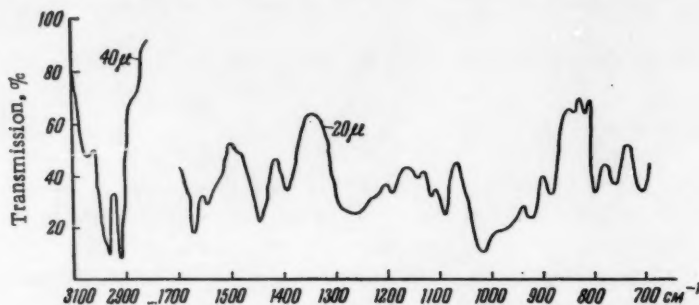


Fig. 2. Infrared spectrum of the chloride of (2-chloromethyl-3-chlorobutadiene-1,3)-4-phosphinic acid.

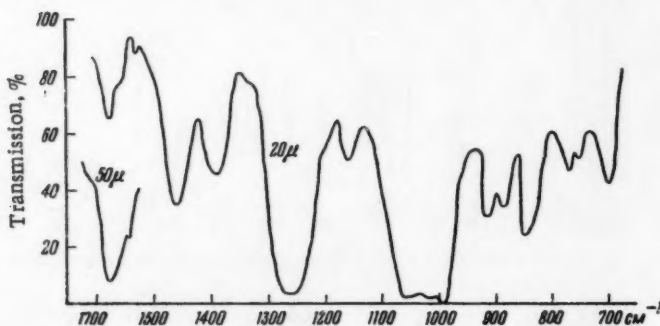


Fig. 3. Infrared spectrum of the di-n-propyl ester of (2-chloromethyl-3-chlorobutadiene-1,3)-4-phosphinic acid.

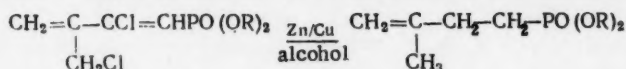
In the case of the compound investigated by us, the intensity of the  $1645\text{ cm}^{-1}$  band amounted to 180 units, i.e., conjugation was also partly interfered with, so that one cannot consider the vibration of the conjugated chain as a whole in the molecule in question. Under the circumstances the strong band in the infrared spectrum must be ascribed essentially to vibrations of the double bond at the end of the molecule, and the weak band at  $1587\text{ cm}^{-1}$  to vibrations of the double bond in the middle of the chain, the frequency of which is lowered considerably because of the effect of the adjacent chlorine and phosphorus atoms and because of partial conjugation with the second double bond.

The fact that one of the hydrogen atoms in the side branch methyl group was substituted by chlorine could be demonstrated by us on the basis of measurements of CH valency frequencies in the spectrum of the molecule. As has been mentioned already, a  $\text{CH}_3$  group gives rise to the two bands at  $2960\text{ cm}^{-1}$  and  $2872\text{ cm}^{-1}$  in the infrared spectrum. These bands were absent in the spectrum of our compound. According to work by Sushchinskii [18], the lines at  $2967$ ,  $2938$ , and  $2879\text{ cm}^{-1}$  in the Raman spectrum are associated with valency vibrations of CH bonds in  $\text{CH}_3$  groups. The  $2938\text{ cm}^{-1}$  and  $2879\text{ cm}^{-1}$  lines were absent in the Raman spectrum of the acid chloride investigated by us. All of this indicated the absence of a methyl group in the compound in question. The positions of the chlorine atoms in the molecule were proved by the distinct measurement of the frequency corresponding to the vinyl

group and the finding of the valency vibration of the chloromethyl group. The absorption bands corresponding to vibrations of the phosphorus groups were in close agreement with the assumed structure of the compound.

The spectra of the di-n-propyl ester of (2-chloromethyl-3-chlorobutadiene-1,3)-4-phosphinic acid were also determined (Fig. 3). Just as in the case of the spectrum of the chloride of this acid, the results obtained showed the presence of the  $880\text{ cm}^{-1}$  group, which is characteristic for vibrations of the vinylidene group, and of the bands at  $1650$  and  $1587\text{ cm}^{-1}$ , which are characteristic for a system of conjugated bonds, the frequency of the vibration of one of which is lowered considerably due to the effect of a chlorine atom located directly at the double bond ( $-\text{CCl}=\text{CH}-$ ).

To prove chemically the structure of the esters of (2-chloromethyl-3-chlorobutadiene-1,3)-4-phosphinic acid, we carried out the reaction of replacement of chlorine with hydrogen (elimination reaction) [19]:



However, this reaction did not take the precise course which we expected. In addition to replacement of chlorine with hydrogen, there was hydrogenation in the middle of the molecule of the double bond next to which chlorine was located. The compound  $\text{CH}_2=\text{C}-\text{CH}_2\text{CH}_2\text{PO}(\text{OR})_2$  was isolated.



The compound obtained was characterized by analyzing it and by determining its molecular refraction and infrared spectrum. As can be seen from Fig. 4, the spectrum had in the region of vibrations of  $\text{C}=\text{C}$  bonds a single strong band at  $1650\text{ cm}^{-1}$ , which is characteristic for an isolated double bond. The presence of a band characteristic for the vinylidene grouping, of a  $\text{P}=\text{O}$  valency vibration, and of bands corresponding to deformational vibrations that are typical for CH frequencies of an ethyl ester, confirm the correctness of the structure which has been formulated.

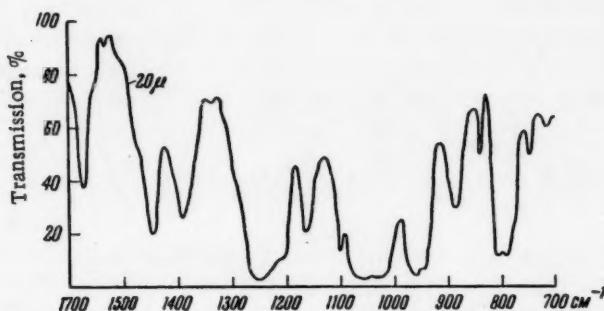


Fig. 4. Infrared spectrum of the diethyl ester of (2-methylbutene-1)-4-phosphinic acid.

## EXPERIMENTAL

Reaction of the addition of  $\text{PCl}_5$  to isopropenylacetylene. The conditions under which this reaction is carried out have been described in a previous communication [20]. After the product of the reaction of  $13.2\text{ g}$  ( $0.2\text{ M}$ ) of isopropenylacetylene with  $83.3\text{ g}$  ( $0.4\text{ M}$ ) of phosphorus pentachloride in  $130\text{ ml}$  of dry and pure benzene at  $0-5^\circ$  had been treated by passing a stream of  $\text{SO}_2$  through the reaction mixture,  $40.8\text{ g}$  of substance was separated. The product obtained was subjected to vacuum distillation, whereupon two fractions were isolated; fraction I,  $7.0\text{ g}$  (yield  $16.7\%$ ); b. p.  $60^\circ$  ( $3\text{ mm}$ );  $\text{CH}_2-\text{CCl}-\text{CCl}=\text{CHCl}$ ; mol. wt.  $208$ ,  $n_D^{20}$   $1.5191$ ;  $d_4^{20}$   $1.4962$ ; found MR  $44.22$ ;



calculated MR  $44.29$ . Found: C  $29.04$ ,  $28.96$ ; H  $2.83$ ,  $2.93$ ; Cl  $68.46$ ,  $68.56\%$ .  $\text{C}_5\text{H}_5\text{Cl}_4$ . Calculated: C  $28.84$ ; H  $2.88$ . Cl  $68.26\%$ , and fraction II,  $29.7\text{ g}$  (yield  $59\%$ ); b. p.  $121^\circ$  ( $3\text{ mm}$ );  $\text{CH}_2=\text{C}-\text{CCl}-\text{CHPOCl}_2$ ; mol. wt.  $254.9$ ;  $n_D^{20}$



$1.5405$ ,  $d_4^{20}$   $1.5400$ ; found MR  $51.75$ ; calculated MR  $52.14$ . Found: C  $23.55$ ,  $23.34$ ; H  $1.82$ ,  $1.82$ ; P  $12.17$ ,  $12.10$ ; Cl  $55.87$ ,  $55.85\%$ .  $\text{C}_5\text{H}_5\text{Cl}_4\text{PO}$ . Calculated: C  $23.56$ ; H  $1.95$ ; P  $12.20$ ; Cl  $55.90\%$ .

Esters of (2-chloromethyl-3-chlorobutadiene-1,3)-4-phosphinic acid. All esters were prepared by a method which had already been described by us [21].

The dimethyl ester of (2-chloromethyl-3-chlorobutadiene-1,3)-4-phosphinic acid was prepared by reacting 12.7 g of the chloride of (2-chloromethyl-3-chlorobutadiene-1,3)-4-phosphinic acid with 6 g of absolute methyl alcohol in the presence of 7.9 g of pyridine. The yield of this substance was 8.5 g (69% of theory), b. p. 136° (3 mm);  $n_D^{20}$  1.4957,  $d_4^{20}$  1.3155; found MR 54.36; calculated MR 54.17. Found: C 34.27, 34.17; H 5.09, 5.00; P 12.75; 12.76%.  $C_7H_{11}Cl_2PO_3$ . Calculated: C 34.28; H 4.49; P 12.65%.

The diethyl ester of (2-chloromethyl-3-chlorobutadiene-1,3)-4-phosphinic acid was prepared by adding 12.74 g of (2-chloromethyl-3-chlorobutadiene-1,3)-4-phosphinic acid chloride to 6 g of absolute ethyl alcohol and 7.9 g of pyridine. The yield of the diethyl ester was 10 g (73% of theory), b. p. 142.5° (2 mm);  $n_D^{20}$  1.4838,  $d_4^{20}$  1.2365; found MR 62.15; calculated MR 63.41. Found: P 11.74, 12.01; Cl 25.34, 25.79%.  $C_9H_{15}Cl_2PO_4$ . Calculated: P 11.32; Cl 25.97%.

The di-n-propyl ester of (2-chloromethyl-3-chlorobutadiene-1,3)-4-phosphinic acid was prepared by adding gradually 38.2 g of the chloride of (2-chloromethyl-3-chlorobutadiene-1,3)-4-phosphinic acid to 18 g of n-propyl alcohol and 23.7 g of pyridine in a benzene solution. The yield was 30.5 g of the di-n-propyl ester (67.5% of theory), b. p. 141° (2 mm);  $n_D^{20}$  1.4805,  $d_4^{20}$  1.1749; found MR 72.78; calculated MR 72.65. Found: C 43.36, 43.56; H 6.46, 6.56; Cl 23.58, 23.35%.  $C_{11}H_{19}PO_3$ . Calculated: C 43.86; H 6.32; Cl 23.53%.

Replacement of chlorine at the double bond with hydrogen (reaction of chlorine elimination). Into a 250 ml 3-neck flask equipped with a mechanical agitator, a condenser, and a tube to let out gas, 5 g of diethyl ester of (2-chloromethyl-3-chlorobutadiene-1,3)-4-phosphinic acid, 6 g of activated zinc dust, 100 ml of 96% ethyl alcohol, and a few small crystals of hydroquinone were placed. The reaction mixture was boiled for 2 hr. During the reaction a rapid stream of nitrogen was passed through the mixture. After completion of the reaction the solution was filtered through a suction funnel. The filtrate contained zinc chloride, which would have brought about polymerization of the product. For this reason the reaction mixture was diluted with 500 ml of water. The reaction product was extracted by shaking out repeatedly with ether. The ether solution was dried with sodium sulfate. The ether and alcohol were evaporated in vacuum. The high-boiling residue was fractionated in vacuum, whereupon 4.5 g of  $CH_2=C(CH_3)CH_2CH_2PO(OC_2H_5)_2$  was obtained, b. p. 70° (15 mm);  $n_D^{20}$  1.4420,  $d_4^{20}$  1.0094; found MR 54.60; calculated MR 54.15. Found: C 52.10, 52.03; H 9.34, 9.42; P 14.86, 14.79%.  $C_9H_{19}PO_3$ . Calculated: C 52.42; H 9.22; P 15.00%.

Determination of infrared spectra. Determination of the spectra in the infrared region was carried out by means of a Hilger D-209 spectrometer, using a single-ray modification of this type of instrument. As the source of light a celite rod with a glow temperature of 1140° was used. Determinations in the region of 4.0-15  $\mu$  were conducted with a sodium chloride prism. Sodium chloride plates served as cuvettes. The thickness of the layer of the substance being investigated was adjusted by interlaying with aluminum foil. This thickness was either 10.30  $\mu$  or 70  $\mu$ .

#### SUMMARY

1. The reaction of the addition of phosphorus pentachloride to isopropenylacetylene was investigated. As products of this reaction the polychlorinated compound 1,2,3,4-tetrachloro-2-methylbutene-4, and the chloride of (2-chloromethyl-3-chlorobutadiene-1,3)-4-phosphinic acid were obtained.
2. By reacting alcohols with (2-chloromethyl-3-chlorobutadiene-1,3)-4-phosphinic acid chloride, the dimethyl, diethyl, and di-n-propyl esters of (2-chloromethyl-3-chlorobutadiene-1,3)-4-phosphinic acid were prepared.
3. Investigation of the infrared spectra of the compounds synthesized confirmed their structure and showed that the frequencies of valency vibrations of CH bonds are increased, and the frequency of the valency vibration of the C=C bond is decreased, as a result of the effect exerted by adjacent chlorine atoms.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

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## INFRARED SPECTRA OF SOME DERIVATIVES OF UNSATURATED PHOSPHINIC ACIDS

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With the purpose of investigating the structure of some derivatives of unsaturated phosphinic acids, we subjected to study their infrared spectra. The investigation conducted made it possible to confirm the structural formulas of compounds that have been synthesized [cf. 1] and to draw some conclusions concerning the mutual influence exerted by atoms and groups in the molecules of the compounds in question.

### EXPERIMENTAL

The spectra were taken on a Hilger D-209 infrared spectrometer of the single-ray type equipped with a sodium chloride prism. Measurement of the spectra was conducted in cuvettes of variable thickness. The thickness of the layer of substance investigated was varied by using aluminum foil interlays of different thickness, from 10 to 40  $\mu$ . In some cases measurements were carried out in a cuvette without an interlay; in these cases the layer was very thin, thinner than 10  $\mu$ . More precise measurements of the thickness of the layer of substance in the cuvette were not made.

### DISCUSSION OF EXPERIMENTAL RESULTS

The table lists those bands of infrared spectra on the basis of which conclusions were made in regard to the structures of the substances investigated. The alkyl radicals of the phosphinic acid derivatives in question differed essentially as far as the position and number of carbon-carbon double bonds (C=C) were concerned. For this reason, examination of the spectral absorption bands characteristic for different types of double bonds made it possible to determine the structure of the alkyl radicals.

In the spectra of the diethyl ester of (2-methylbutene-2)-4-phosphinic acid (I), the diethyl ester of (3-chloro-2-methylbutene-2)-4-phosphinic acid (II), the chloride of (3-chloro-2-methylbutene-2)-4-phosphinic acid (III), and the di-n-propyl ester of (3-chlorobutene-2)-4-phosphinic acid (IV) there are absorption bands of medium intensity in the 1650-1660  $\text{cm}^{-1}$  range (cf. Fig. 1).

These bands are associated with C=C bonds in the molecules of the compounds mentioned, because one usually finds in the range of 1650-1660  $\text{cm}^{-1}$  absorption bands which correspond to valency vibrations of double bonds of the

types of  $\text{CH}_2=\text{CHR}$  and  $\text{CH}_2=\text{C} \begin{smallmatrix} \text{R} \\ \diagup \\ \text{R} \end{smallmatrix}$  in olefins [2]. The frequency of the valency vibration of the double bond in

the ester (II) was found to be lower than the frequency of the vibration of this bond in ester (I). This difference can be ascribed to the effect of the chlorine atom bound to the carbon that is adjacent to the double bond in ester (II). However, one cannot regard as established that chlorine exerts this effect on vibrations of a double bond, because the observation in question was made on two substances only, i.e., the esters (I) and (II). On the other hand, it is known [3] that when a chlorine atom is located directly at a double bond, the frequency of the vibration of this bond is strongly reduced.

In 870-910  $\text{cm}^{-1}$  range of the spectra of the compounds mentioned, absorption bands were observed which correspond to deformational vibrations of CH at the C=C double bond, and can be regarded as a reliable criterion for

| Number of substance | Name of substance  | $\nu_{C=C}$      | $\nu_{P=O}$ | C-O in P-O-C group | $\delta_{CH}$ at C-C                                 | $\nu_{P-C}$ in P-O-C  |
|---------------------|--|------------------|-------------|--------------------|--|-----------------------|
| I                   | Diethyl ester of (2-methylbutene-2)-4-phosphinic acid<br>$CH_2=C(CH_3)-CH_2-CH_2-PO(OC_2H_5)_2$          | 1650 m*          | 1250 v.l.   | 1056-1025 v.l.     | 888 m  | 790 l, 750 l          |
| II                  | Diethyl ester of (3-chloro-2-methylbutene-2)-4-phosphinic acid<br>$CH_2=C(CH_3)-CHCl-CH_2-PO(OC_2H_5)_2$ | 1660 m           | 1250 v.l.   | 1060-1020 v.l.     | 872 m  | 800 l, 725 l          |
| III                 | Chloride of (3-chloro-2-methylbutene-2)-4-phosphinic acid<br>$CH_2=C(CH_3)-CHCl-CH_2-POCl_2$             | 1660 m           | 1260 v.l.   |                    | 872 m  | 800 l, 740 l.         |
| IV                  | Di-n-propyl ester of (3-chlorobutene-2)-4-phosphinic acid<br>$CH_2=CH-CHCl-CH_2-PO(OC_3H_7)_2$           | 1650 m           | 1250 v.l.   | 1075-950 v.l.      | 910 l  | 750 m                 |
| V                   | Chloride of vinylphosphinic acid<br>$CH_2=CHPOCl_2$  | 1605 l           | 1270 v.l.   |                    | (980 l)**  | 740 l                 |
| VI                  | Diethyl ester of vinylphosphinic acid<br>$CH_2=CHPO(OC_2H_5)_2$  | 1611 m           | 1250 v.l.   | 1050-1030 v.l.     | Not detected because of superposition of other bands | 790 l, 720 m          |
| VII                 | Diethyl ester of (butadiene-2,4)-4-phosphinic acid<br>$CH_2=CH-CH=CH-PO(OC_2H_5)_2$                      | 1640 m<br>1590 l | 1250 v.l.   | 1060-1020 v.l.     |  | 790 l, 740 l<br>750 m |
| VIII                | Di-n-propyl ester of (butadiene-2,4)-4-phosphinic acid<br>$CH_2=CH-CH=CH-PO(OC_3H_7)_2$                  | 1640 m<br>1590 l | 1250 v.l.   | 1075-980 v.l.      | (864)**  | 800 l, 750 m          |
| IX                  | Diethyl ester of (2-methylbutadiene-2,4)-4-phosphinic acid<br>$CH_2=C(CH_3)-CH=CH-PO(OC_2H_5)_2$         | 1630 l<br>1585 l | 1250 v.l.   | 1060-1030 v.l.     |  |                       |

\* The frequencies are given in  $cm^{-1}$ . The intensities of the bands are indicated as follows: v.l. - very intense; i - intense; m - of medium intensity; l - of low intensity.

\*\* Absorption bands, the correlation of which is doubtful, are listed in parentheses.

the presence of a vinyl group in ester (IV)\* (the band at  $910\text{ cm}^{-1}$ ) and of vinylidene groups in ester (I) (band at  $888\text{ cm}^{-1}$ ), ester (II) (band at  $872\text{ cm}^{-1}$ ), and the chloride (III) (band at  $872\text{ cm}^{-1}$ ).

The shift in the spectrum of ester (II) of the absorption band corresponding to the vinylidene group towards a lower frequency ( $872\text{ cm}^{-1}$ ) as compared with the position of this band ( $888\text{ cm}^{-1}$ ) in the spectrum of ester (I) presumably takes place because of the effect of the adjacent chlorine atom.

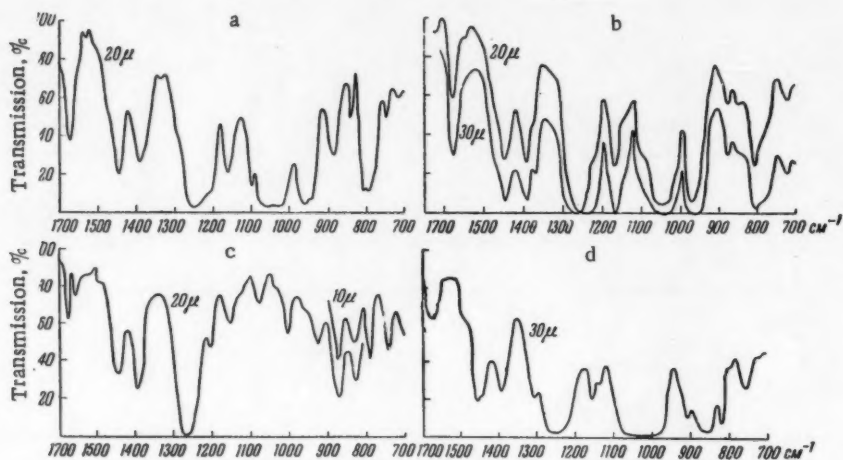


Fig. 1. Infrared spectra of a) diethyl ester of (2-methylbutene-2)-4-phosphinic acid; b) diethyl ester of (3-chloro-2-methylbutene-2)-4-phosphinic acid; c) chloride of (3-chloro-2-methylbutene-2)-4-phosphinic acid; d) di-n-propyl ester of (3-chlorobutene-2)-4-phosphinic acid.

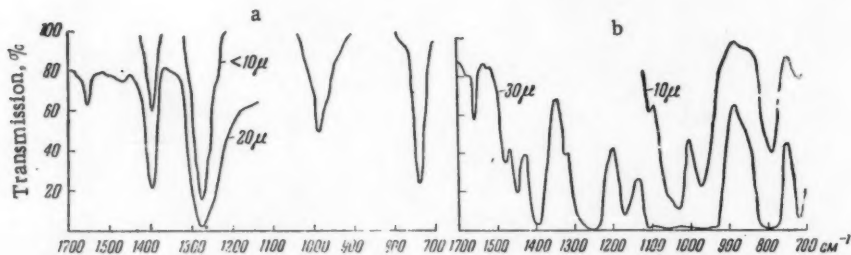


Fig. 2. Infrared spectra of a) chloride of vinylphosphinic acid; b) diethyl ester of vinylphosphinic acid.

In order to establish the effect of the phosphinic acid group on the double bond  $\text{C}=\text{C}$ , the spectra of the diethyl ester and chloride of vinylphosphinic acid (V and VI) were investigated. In the spectrum of the ester (cf. Fig. 2b) the frequency of the valency vibration of the double bond was lowered by approximately  $40\text{ cm}^{-1}$  as compared with the frequency of the vibration of the double bond in ester (IV), where the  $\text{C}=\text{C}$  bond is not conjugated with the phosphinic acid group. The frequency of the valency vibration of the  $\text{C}=\text{C}$  bond in the chloride of vinylphosphinic acid (cf. Fig. 2a) was lowered by an additional  $5\text{ cm}^{-1}$  as compared with the frequency of this vibration in the ester of the same acid.

In the case of conjugation of  $\text{C}=\text{C}$  double bonds with a carbonyl group, strong lowering of the frequencies of vibration of both the  $\text{C}=\text{C}$  double bond and the carbonyl bond takes place. For instance, as a result of conjugation in methacrylic acid esters both the  $\text{C}=\text{O}$  band and the  $\text{C}=\text{C}$  band are displaced by approximately  $15\text{ cm}^{-1}$  into the

\*The presence of a  $\text{C}=\text{C}$  bond at the end of the molecule of ester (IV) was also confirmed by the fact that formic acid was obtained as a result of the action of ozone on this ester.

region of smaller wave numbers [4]. However, our data show that conjugation with double bonds does not affect the frequency of vibration of the P=O bond. One must note that in carboxylic acid derivatives in which the C=O bond is conjugated with a C=C bond, both conjugated bonds are in the same plane, which contributes to a maximum degree of interaction between the electronic clouds of these bonds. In analogous derivatives of phosphinic acids the C=C bond cannot be located in the same place as the P=O bond because of the different spatial configuration of the P=O group. It follows from this that the strong lowering of the frequency of the double bond in derivatives of vinylphosphinic acid must be ascribed to the effect of the phosphorus atom rather than that of the P=O group as a whole. The effect of the phosphorus must also be noticeable in the deformational vibrations of the CH group at the C=C double bond. It has been found that in spectra of acrylic acid esters bands at 984 and 965  $\text{cm}^{-1}$  are observed instead of the bands at 990 and 910  $\text{cm}^{-1}$ , which are characteristic for the vinyl group in olefins [5]. The strong shift of the 910  $\text{cm}^{-1}$  band takes place because of conjugation between the carbon-carbon double bond and the carbonyl bond. No band in the region of 910  $\text{cm}^{-1}$  has been observed in the spectrum of vinylphosphinic chloride; however, there has been a very strong band at 980  $\text{cm}^{-1}$ , which might be ascribed to deformational vibrations of the vinyl CH that has been strongly excited under the effect of the phosphorus atom next to the vinyl group. Unfortunately, we have not been able to confirm this in the case of the ethyl ester of vinylphosphinic acid, because in the spectrum of this compound there was a very intense band at 960  $\text{cm}^{-1}$ , which is characteristic for ethyl esters of phosphinic acids. This band covered the region of the 980  $\text{cm}^{-1}$  frequency.

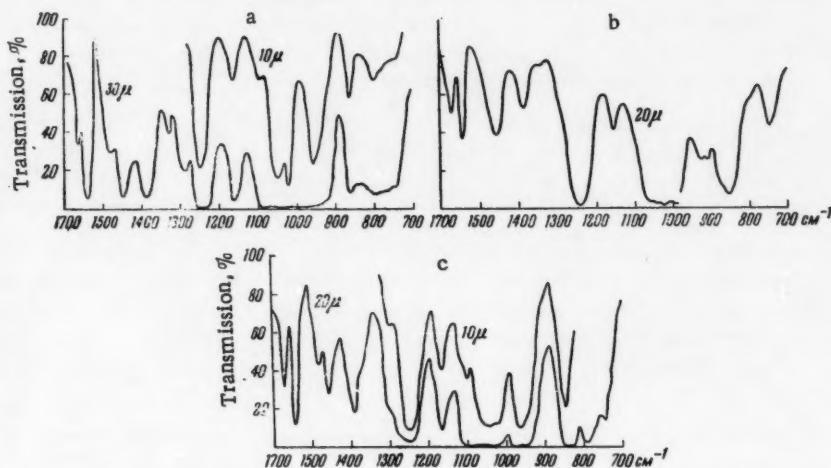


Fig. 3. Infrared spectra of a) diethyl ester of (butadiene-2,4)-4-phosphinic acid; b) di-n-propyl ester of (butadiene-2,4)-4-phosphinic acid; c) diethyl ester of (2-methylbutadiene-2,4)-4-phosphinic acid.

In the spectra of the diethyl and di-n-propyl esters of (butadiene-2,4)-4-phosphinic acid (VII and VIII) and the diethyl ester of (2-methylbutadiene-2,4)-4-phosphinic acid (IX), two absorption bands in the 1585-1640  $\text{cm}^{-1}$  region were found in every case (Fig. 3). Two absorption bands in this region are observed in spectra of dienes with conjugated double bonds; these bands correspond to symmetric and antisymmetric vibrations of the system of conjugated double bonds [6]. In the infrared spectrum of a symmetric molecule like butadiene there is only a single absorption band at 1599  $\text{cm}^{-1}$ , which corresponds to the antisymmetric vibration of the double bonds; the symmetric vibration is inactive and does not show in the infrared spectrum. But already in the infrared spectrum of pentadiene there are two absorption bands (at 1661 and 1610  $\text{cm}^{-1}$ ) in the case of the trans-isomer, and at 1656 and 1600  $\text{cm}^{-1}$  in the case of the cis-isomer [7], while the spectrum of isoprene shows bands at 1650 and 1605  $\text{cm}^{-1}$ .

In the spectra of esters (VII) - (IX) the relative intensity of the bands in this region was found to be the same as in the spectra of pentadiene and isoprene: The bands in the region of lower wave numbers were strong and those in the region of higher wave numbers were relatively weak. This comparison gives reasons to believe that the double bonds in the compounds in question are located similarly to those in pentadiene and isoprene, and furthermore makes it possible to ascribe by analogy the bands under consideration to symmetric and antisymmetric vibrations of a

system of conjugated C=C double bonds, respectively. However, the position of the bands in the spectra of esters (VII) - (IX) was displaced towards the region of lower wave numbers by approximately 15-20  $\text{cm}^{-1}$  as compared with the position of these bands in the spectra of pentadiene and isoprene. This displacement can only be explained by the effect of the neighboring phosphorus atom. The frequencies of deformational vibrations of CH at double C=C bonds in the esters (VII), (VIII), and (IX) must also be greatly changed, because no absorption bands in the corresponding regions (910  $\text{cm}^{-1}$  for the vinyl group and 888  $\text{cm}^{-1}$  for the vinylidene group) were observed in the spectra of these esters. However, no conclusions could be made in regard to the magnitude of the displacement of these bands because of the presence in neighboring regions of the spectrum of absorption bands characteristic for other structural groups in the molecules of the esters in question.

In the spectra of all phosphinic acid derivatives investigated by us there were very intense absorption bands in the 1250-1270  $\text{cm}^{-1}$  region, which undoubtedly are indicative of the presence of the P=O bond in the compounds in question, because according to data reported by a number of investigators [8-9] the absorption bands corresponding to the valency vibration of this bond are located in the region of 1200-1300  $\text{cm}^{-1}$ . In the spectra of the acid chlorides (III) and (V) the bands corresponding to the P=O bond were located in the region of 1270  $\text{cm}^{-1}$ , i.e., they were displaced towards higher frequencies by 20  $\text{cm}^{-1}$  as compared with the position of these bands in the spectra of the esters of the corresponding acids. This displacement of the absorption bands is presumably due to a shift in the electron density of the P=O bond induced by the effect of the chlorine atom. The effect of chlorine on the frequency of the P=O bond vibration is weaker than its effect on the frequency of the vibration of the C=O bond in the corresponding chlorides of carboxylic acids. Thus, in esters of saturated carboxylic acids [10] the C=O bond frequency amounts to 1735  $\text{cm}^{-1}$ , and in the chlorides of the same acids to 1810  $\text{cm}^{-1}$ , i.e., it is increased by 75  $\text{cm}^{-1}$ . One may assume that in phosphinic acid derivatives the electron shell of the phosphorus partially screens the P=O bond from the effects exerted by adjacent atoms and groups.

The strong doublet absorption bands in the 1000-1060  $\text{cm}^{-1}$  range of the spectra of the phosphinic acid esters which were investigated must be ascribed to vibrations of the O-C bond in the P-O-C group [9]. In the spectra of ethyl esters of the different phosphinic acids, the doublet maxima were found to be located at approximately 1060 and 1030  $\text{cm}^{-1}$ , whereas in the spectra of the propyl esters the positions of these maxima were at 1070 and 1000  $\text{cm}^{-1}$ .

As has already been noted, strong absorption bands in the region of 960  $\text{cm}^{-1}$  were observed in the spectra of ethyl esters of all phosphinic acids with different alkyl radicals that have been investigated by us (e.g., the spectra of esters I, II, VI, VII, and IX), while no bands in this region were present in the spectra of propyl esters. It follows from this that a band at 960  $\text{cm}^{-1}$  is typical for an ethoxy group bound to phosphorus.

#### SUMMARY

1. The structure of nine derivatives of unsaturated phosphinic acids has been established.
2. It has been shown that under the effect of an adjacent phosphorus atom the frequencies of valency vibrations of C=C bonds are strongly lowered and the frequency of the deformational vibration of the C-H bond at C=C double bonds is changed.

Conjugation with C=C bonds does not exert a noticeable effect on the frequency of the vibration of the P=O group. In phosphinic acid chlorides the frequency of the valency vibration of the P=O bond is increased by 20  $\text{cm}^{-1}$  under the effect of chlorine atoms.

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# THE REACTION OF FERROCENE DERIVATIVES WITH ARYLDIAZONIUMS

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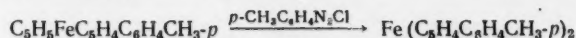
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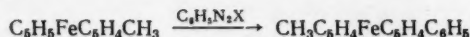
Ferrocene reacts with arylldiazoniums with formation of arylferrocenes, as has been shown previously by us [1-3], and also by Broadhead and Pauson [4]. Arylation of ferrocene as the ferricinium cation was accomplished by Weinmayr [5]. Mono- and diarylferrocenes are the main products of ferrocene arylation. The aryl groups in the diarylferrocenes so obtained are located in different cyclopentadienyl rings [4, 6, 7]. Only by the reaction of *p*-anisylldiazonium on ferrocene is homoannular dianisylferrocene formed, in low yield, as shown by Broadhead and Pauson [4]. These authors found that monophenylferrocene is arylated by phenylldiazonium, giving heteroannular diphenylferrocene [4].

In the present work we investigated arylation of *p*-tolyl-, methyl- and ethylferrocene, and also acyl- and carboxyferrocenes. We found that *p*-tolylferrocene is arylated by *p*-tolylldiazonium, giving heteroannular di-(*p*-tolyl)ferrocene in 9% theoretical yield.



Change in experimental conditions did not lead to an increased yield. Evidently, one of the factors causing a low yield of di-(*p*-tolyl)ferrocene, besides the low activity of *p*-tolylldiazonium, observed in the synthesis of unsymmetric diaryls [8], is that of the properties of the resulting di-(*p*-tolyl)ferrocene itself. During decomposition, the di-(*p*-tolyl)ferricinium cation appeared to be one and a half times more unstable than the *p*-tolylferricinium cation. It is possible that the product formed as a cation decomposes in acid solution. This theory agrees with the fact that we were unsuccessful in obtaining di-(*p*-tolyl)ferrocene on arylating the *p*-tolylferricinium cation, whereas a high yield of *p*-tolylferrocene itself is obtained under these conditions.

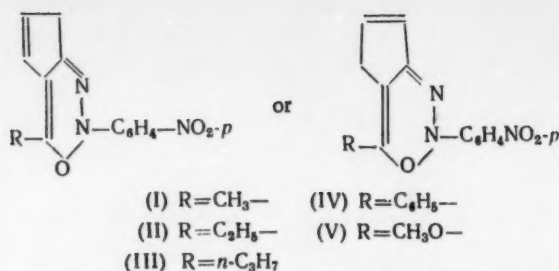
On reacting methylferrocene with phenylldiazonium, a mixture of phenylated methylferrocenes was obtained, from which a low yield of heteroannular methylphenylferrocene was isolated.



On arylating ethylferrocene with phenylldiazonium, a mixture of ethylferrocene phenylation products was also obtained, from which a 21% yield of monophenylated ethylferrocene was isolated by chromatography, the latter compound being heteroannular ethylphenylferrocene with a small trace of homoannular isomer. The trace was observed spectroscopically, and also in preparation of small amounts of pentabromocyclopentane after treatment with bromine.

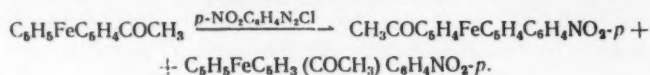
1,1'-Diacylferrocene reacts with diazo compounds, as has been communicated by us previously [9], in contrast to ferrocene, with rupture of the ferrous bonds with the cyclopentadienyl rings, forming compounds which are, as we have shown [10], derivatives of a 1,2,3-oxadiazine (I).

In the present work we investigated the reaction of heteroannular dipropionyl-, dibutyryl-, and dibenzoylferrocene with *p*-nitrophenylldiazonium. The reaction proceeds as that with diacetylferrocene but less smoothly: Part of the dipropionyl- and dibutyrylferrocene is recovered unchanged, considerable resinification occurs, and yield of compounds containing no iron are appreciably lower (1-3%). By analogy with the substances formed from 1,1'-diacetylferrocene, the structure of which has been demonstrated by us [10], it could be considered that these compounds also are 1,2,3-oxadiazine derivatives (II, III, IV).

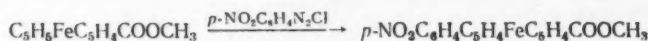


We investigated also the reaction of p-nitrophenyldiazonium with the dimethyl ester of ferrocenedicarboxylic acid. The reaction was accompanied by considerable resinification. After careful chromatography on aluminum oxide we succeeded in isolating a low yield of p-nitrophenyldicarbomethoxyferrocene, rupture of the ferrocene nucleus also occurring, as evidenced by the observation of ionic iron. A slight amount also of a substance was isolated, corresponding approximately in composition to p-nitrophenylazocarbomethoxycyclopentadiene, and evidently having structure (V). This substance chromatographed and crystallized poorly, and could not be obtained in pure form.

The monosubstituted ferrocenes — acetylferrocene and carbomethoxyferrocene react with p-nitrophenyldiazonium similarly to ferrocene, but yields of arylation products are considerable lower. Monoacetylferrocene forms on reacting with p-nitrophenyldiazonium both homo- and heteroannular p-nitrophenylacetylferrocene



On reacting the methyl ester of ferrocenecarboxylic acid with p-nitrophenyldiazonium, arylation of the free cyclopentadienyl ring occurs and heteroannular p-nitrophenylcarbomethoxyferrocene is formed; yield 7%



The presence or absence of an unsubstituted cyclopentadienyl ring was demonstrated spectroscopically in every case.

Free mono- and dicarboxylic acids of ferrocene and their sodium salts on reacting with p-nitrophenyldiazonium give a complex mixture of substances, from which arylation products cannot be isolated. In this respect the behavior of ferrocenecarboxylic acids is similar to the behavior of benzoic acid in the Homberg reaction [8].

## EXPERIMENTAL

**Preparation of p-Tolylferrocene.**\*\* 50 g (0.27 M) of ferrocene was dissolved with cooling in 136 ml of concentrated sulfuric acid. The solution was left overnight, then poured with stirring into ice; to this was added a solution of p-tolyldiazonium chloride, prepared from 29 g (0.27 M) of p-toluidine. The reaction mixture was stirred for 8 hr, then left overnight. The dark-brown precipitate settling out was filtered off, washed with water, and air-dried. The aqueous solution was reduced with stannous chloride, the precipitate filtered off, and from it unreacted ferrocene driven off by steam distillation (14 g, 28% on that used in the reaction). The precipitate was separated from the water, united with the precipitate\*\*\* isolated earlier, and extracted in a Soxhlet apparatus with petroleum ether, 45 g (62% theoretical) of p-tolylferrocene was obtained with m. p. 110-112°. After chromatography on aluminum oxide and recrystallization from alcohol, m. p. was 139-140°. The p-tolylferrocene thus prepared was identical with that obtained by us previously [2] by arylating ferrocene in an aqueous-ethereal medium.

**Arylation of p-Tolylferrocene.** To a solution of 8 g (0.03 M) of p-tolylferrocene in 300 ml of glacial acetic acid cooled to 0°, was added an aqueous solution of p-tolyldiazonium chlorides, prepared\*\*\*\* from 3.2 g (0.03 M) of p-toluidine. The reaction mixture was stirred for 2 hr with cooling to 0-5°, then reduced with stannous chloride.

\* Position of the double bonds has not been established.

\*\* Preparation of p-tolylferrocene and its arylation was carried out with the cooperation of L. V. Ershova.

\*\*\* In one of the experiments, p-tolylferrocene formed in the unoxidized form and the cation was prepared separately. It appeared that amounts of this and the other were approximately equal.

\*\*\*\* In this and in all subsequent syntheses in aryldiazonium formation, unreacted nitrous acid was removed by addition of urea, and the mineral acid made neutral to Congo red with sodium acetate.

The precipitate was filtered off, washed with water, air-dried, and extracted with petroleum ether in a Soxhlet apparatus. After partial removal of petroleum ether and subsequent recrystallization from alcohol, 1 g (9% theoretical) of di-(p-tolyl)ferrocene was obtained; m. p. 168-169°. Found: C 79.11, 79.09; H 6.13, 6.04%.  $C_{24}H_{22}Fe$ . Calculated: C 78.70; H 6.05%. In the i.r. - spectrum of di-(p-tolyl)ferrocene, frequencies in the region 1000 and 1100  $cm^{-1}$  were absent.

On further evaporation of petroleum ether, 3.1 g of unreacted p-tolylferrocene was obtained (38% of that used in the reaction). Yield of di-(p-tolyl)ferrocene, calculated on p-tolylferrocene entering the reaction, was 15% theoretical. Use of excess p-tolyldiazonium did not lead to increase in di-(p-tolyl)ferrocene yield, and conducting the reaction at room temperature lowered the yield sharply.

In another experiment, conducted under the same conditions, reduction with stannous chloride was omitted, and the reaction mixture extracted with ether. It appeared that all the di-(p-tolyl)ferrocene passed into the ether, and after reduction of the remaining acetic acid solution with stannous chloride, only the initial p-tolylferrocene was obtained. Consequently, all the di-(p-tolyl)ferrocene was obtained in the unoxidized form, this possibly being caused by the low stability of its cation.

On reacting the p-tolylferricinium cation with p-tolyldiazonium, it was found impossible to obtain di-(p-tolyl)ferrocene. After reduction of the reaction mixture, only the initial p-tolylferrocene was obtained (3 g of the 8 g used in the reaction).

Arylation of methylferrocene. To a solution of 2 g (0.01 M) of methylferrocene [11] and 8 g of sodium acetate in glacial acetic acid was slowly added with stirring a solution of phenyldiazonium sulfate, prepared from 0.93 g (0.01 M) of aniline. Stirring was continued at room temperature for 1.5 hr, and the mixture then diluted with 100 ml of water and extracted with benzene. The benzene extracts were washed with 2 N caustic solution and water, dried with  $CaCl_2$  and chromatographed on aluminum oxide. Washing out was effected with petroleum ether. On chromatography, 3 bands were obtained on the column. From the first band was obtained 0.42 g of initial methylferrocene (21% of the amount used in the reaction), from the second - 0.15 g (yield 5.4% theoretical) of methylphenylferrocene, an orange, crystalline substance; m. p. 88-89° (from petroleum ether). Found: C 74.17, 74.13; H 5.88, 5.87; Fe 19.60, 19.80%.  $C_{17}H_{16}Fe$ . Calculated: C 73.92; H 5.83; Fe 20.25%.

In the i.r.-spectrum of methylphenylferrocene, frequencies in the region 1000 and 1100  $cm^{-1}$  were absent, hence the methyl and the phenyl groups are located in different cyclopentadienyl rings.

After washing out the third band, an orange, crystalline substance was obtained with m. p. 150-152°. From its analysis by elements, this was a mixture of tri- and tetraphenylated methylferrocene. Found: C 82.11; H 5.66%.

Arylation of ethylferrocene was carried out under the same conditions as for arylation of methylferrocene, but stirring was continued for 2 hr. From 8.4 g (0.04 M) of ethylferrocene [12] was obtained 3.12 g (yield 20% theoretical) of monophenylated ethylferrocene;  $n_D^{20}$  1.6470,  $d_4^{20}$  1.2367. Found: C 74.77, 74.58; H 6.47, 6.58; Fe 18.72, 19.10%.  $C_{18}H_{18}Fe$ . Calculated: C 74.49; H 6.25; Fe 19.26%.

In the i.r.-spectrum, weak absorption bands were observed in the region 1000 and 1100  $cm^{-1}$ . By the action of bromine [13] on the ethylphenylferrocene obtained, only a slight amount of pentabromocyclopentane was obtained. Evidently, the trace of homoannular isomer did not exceed several percent.

In addition, 0.4 g of a mixture of polyphenylated ethylferrocenes was obtained. 2.7 g (32%) of initial ethylferrocene was recovered unchanged.

Arylation of 1,1'-dipropionylferrocene. Into a solution of 12 g (0.04 M) of 1,1'-dipropionylferrocene [12] in glacial acetic acid was poured, over a period of 30 min with stirring, a solution of p-nitrophenyldiazonium chloride, prepared from 28 g (0.2 M) of p-nitroaniline. Stirring was then continued for 1 hr 40 min at room temperature and for 1 hr 15 min with heating (45-50°). The resinous precipitate was separated from the solution (the solution gave a reaction for  $Fe^{3+}$ ), washed with water, dried, and extracted in a Soxhlet apparatus, in turn with petroleum ether, a mixture (1:1) of benzene and cyclohexane, and with benzene. All the solutions were washed with 2 N alkali with water, and dried over sodium sulfate. On washing with alkali, formation of a dark-brown precipitate was observed. The solution in petroleum ether was chromatographed on aluminum oxide. 0.9 g of initial ketone was obtained, and a white substance not investigated further.

A red, powdery substance (0.2 g) separated out from the solution in a mixture of benzene and cyclohexane after partial evaporation of solvent. The substance was washed with petroleum ether and four times recrystallized

from benzene; m. p. 175-176°. From the benzene solution after solvent removal was obtained a resinous product, from which after washing with petroleum ether and recrystallizing from benzene was obtained 0.15 g of a substance identical with that obtained from the benzene-cyclohexane extract. The two portions were united and again recrystallized from benzene. A dark-red substance was obtained; it was a substituted 1,2,3-oxadiazine (structure II); m. p. 175-176°; yield 0.35 g (2% theoretical). Found: C 61.49, 61.36; H 4.93, 4.85; N 15.34, 15.22%.  $C_{14}H_{13}N_3O_3$ . Calculated: C 61.98; H 4.83; N 15.49%.

Arylation of 1,1'-dibutyrylferrocene. The reaction was carried out as described for 1,1'-dipropionylferrocene. From 13 g of 1,1'-dibutyrylferrocene [12] 1.5 g of ketone was recovered unchanged, and 0.15 g of a dark-red substance (III), a substituted 1,2,3-oxadiazine, obtained; m. p. 236-237° (with decomposition, in a sealed capillary tube). Found: C 62.50, 62.73; H 5.36, 5.40%.  $C_{15}H_{15}N_3O_3$ . Calculated: C 63.15; H 5.30%.

Arylation of 1,1'-dibenzoylferrocene.\* The reaction was carried out as described for 1,1'-dipropionylferrocene, but heating was continued for 2.5 hr. From 7 g of 1,1'-dibenzoylferrocene [12] was obtained 0.35 g (3% theoretical) of a derivative of a 1,2,3-oxadiazine (IV), which was recrystallized from chloroform and from a mixture of benzene and petroleum ether, and chromatographed on aluminum oxide in a solution of benzene and petroleum ether (1:1); m. p. 220-222° (with decomposition). Found: C 67.55, 67.59; H 4.19, 4.18%.  $C_{18}H_{13}N_3O_3$ . Calculated: C 67.70; H 4.10%.

Arylation of 1,1'-dicarbomethoxyferrocene. To a solution of 6.04 g (0.02 M) of 1,1'-dicarbomethoxyferrocene [14] in glacial acetic acid was added over a period of 10 min with stirring, a solution of p-nitrophenyldiazonium chloride, prepared from 14 g (0.1 M) of p-nitroaniline. The reaction mixture was stirred for 5 hr at room temperature and left overnight. The resinous product was then separated from the solution, washed with water, and dried. The filtrate gave a reaction for  $Fe^{3+}$ .

The reaction products (weight 14.1 g) were then extracted with benzene for 3-4 days and chromatographed on aluminum oxide. The chromatogram was complicated. Several layers developed (from below upwards): 1) yellow; 2) red; 3) crimson; 4) brown; 5) dark-brown. Two substances — a white and a red — were washed out with benzene. The white substance had m. p. 189.5-190.5°, and was not investigated further. Found: C 59.36, 59.13; H 3.89, 3.87%.

The red substance (0.04 g) was obtained by prolonged washing of the column with benzene, and was twice recrystallized from benzene; decomp. temp. 210-230°. On analysis, the substance corresponded approximately to p-nitrobenzeneazocarbomethoxycyclopentadiene, but was probably a derivative of a 1,2,3-oxadiazine (structure V); it could not be obtained in the pure form. Found: C 58.28, 57.94; H 4.00, 3.79; N 13.53, 13.60%.  $C_{13}H_{11}N_3O_4$ . Calculated: C 57.15; H 4.06; N 15.38%.

0.15 g of p-nitrophenyldicarbomethoxyferrocene with m. p. 140-141° (from benzene) was washed from the column with absolute ether. Found: C 56.62, 56.67; H 4.12, 4.18; Fe 13.14, 13.23%.  $C_{20}H_{17}NO_6Fe$ . Calculated: C 56.76; H 4.28; Fe 13.20%.

In addition, the column was washed with a mixture of ether and methyl alcohol, and with acetone, but individual substances could not be obtained from these solutions.

In one of the experiments, the amount of p-nitrophenyldiazonium was decreased by half (for 0.04 M of dicarbomethoxyferrocene 0.1 M of diazo compound was taken). 0.5 g of a white substance of unknown structure was obtained, 0.5 g of initial ether, 0.2 g (1.5%) of p-nitrophenyldicarbomethoxyferrocene with m. p. 140-141°, and 0.015 g of a powdery red substance with m. p. 163-165°, close in composition to p-nitrophenyldicarbomethoxyferrocene, and evidently forming both a 1,2- and a 1,3-isomer. Found: C 56.00, 56.14; H 4.26, 4.21; Fe 13.19%.  $C_{20}H_{17}NO_6Fe$ . Calculated: C 56.76; H 4.28; Fe 13.20%.

Arylation of carbomethoxyferrocene. To a solution of 4.86 g (0.02 M) of the methyl ester of ferrocenecarboxylic acid [1] in 50 ml of glacial acetic acid was added a solution of p-nitrophenyldiazonium chloride, prepared from 5.6 g of p-nitroaniline. Stirring was continued for 1 hr at room temperature. The resinous product was separated from the solution, dissolved in benzene, and chromatographed on aluminum oxide. 0.51 g of p-nitrophenylcarbomethoxyferrocene was washed from the column with benzene, forming dark-red, acicular crystals with m. p. 151-152° (from benzene); yield 7% theoretical. Found: C 59.07, 59.46; H 4.28, 4.17; Fe 15.28, 15.62; N 3.96, 4.12%.  $C_{18}H_{15}NO_4Fe$ . Calculated: C 59.21; H 4.14; Fe 15.30; N 3.84%. In the i.r.-spectrum of the substance there were no frequencies characteristic of the unsubstituted cyclopentadienyl ring.

\* Carried out together with M. Kristynyuk.

Arylation of monoacetylferrocene. The reaction was carried out with 4.56 g of acetylferrocene as described for 1,1'-dipropionylferrocene. Stirring was continued for 1 hr at room temperature and for 2 hr with heating. On chromatographing the benzene solution with benzene with a drop of dioxane, homoannular acetyl p-nitrophenylferrocene was washed out at the beginning, with m. p. 158-160° (with decomposition) after recrystallization from chloroform and methyl alcohol. Found: C 61.80, 61.73; H 4.46, 4.51; Fe 15.59, 15.61; N 4.41, 4.35%.  $C_{18}H_{15}NO_3Fe$ . Calculated: C 61.91; H 4.33; Fe 15.99; N 4.01%.

In the i.r.-spectrum of the substance, bands were observed at 1007 and 1112  $cm^{-1}$ , this indicating the presence of a free cyclopentadienyl ring.

On more prolonged washing with benzene with a very small amount of dioxane was obtained after a second chromatography on aluminum oxide, 0.35 g (yield 5% theoretical) of heteroannular acetyl- p-nitrophenylferrocene, forming a violet-brown, crystalline substance, readily soluble in acetone, chloroform, benzene, less so in petroleum ether, methyl and ethyl alcohols, crystallizing from alcohol, petroleum ether, and n-heptane; m. p. 122-123° (with decomposition). Found: C 61.78, 61.90; H 4.70, 4.53; Fe 15.67, 16.25; N 3.69%.  $C_{18}H_{15}NO_3Fe$ . Calculated: C 61.91; H 4.33; Fe 15.99; N 4.01%.

In the i.r.-spectrum of the substance, bands in the region 1000 and 1100  $cm^{-1}$  were not observed.

#### SUMMARY

1. The reaction of ferrocene derivatives with aryldiazoniums was studied.
2. On arylating p-tolylferrocene with p-tolyldiazonium, 1,1'-di-(p-tolyl)ferrocene was obtained.
3. On reacting methyl- and ethylferrocene with phenyldiazonium, a mixture of arylation products is formed, from which are obtained heteroannular methylphenylferrocene and ethylphenylferrocene.
4. Dipropionyl-, dibutyl-, and dibenzoylferrocene react with p-nitrophenyldiazonium with rupture of the ferrocene nucleus, giving low yields of derivatives on a 1,2,3-oxadiazine.
5. On reacting the dimethyl ester of ferrocenedicarboxylic acid with p-nitrophenyldiazonium, both arylation and rupture of the ferrocene nucleus take place.
6. Monoacetylferrocene and the methyl ester of ferrocenemonocarboxylic acid are arylated on reacting with p-nitrophenyldiazonium.

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## β-LACTAMS

### PART IV. SYNTHESIS OF 3,3-DIPHENYLAZETIDINONES-2

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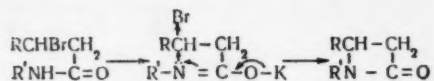
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No. 1, pp. 83-88, January, 1961

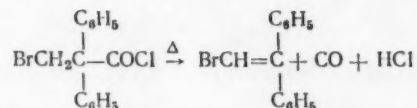
Original article submitted July 16, 1959

We have previously developed a method for the synthesis of β-lactams from the amides of β-bromosubstituted carboxylic acids [1, 2]

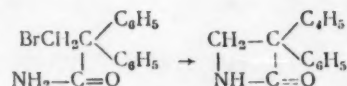


The preparation of lactams from all the amides of β-bromohydrocinnamic acid investigated was accompanied by a side reaction in which unsaturated amides were formed. Naturally it was thought that cyclization of the amides of β-bromosubstituted carboxylic acids which did not have a α-hydrogen should go in one sense only. This cyclization appeared still more interesting because 3-substituted azetidinones-2 are known to be biologically active substances which render the central nervous system passive [3, 4].

The readily accessible amides of α,α-diphenyl-β-bromopropionic acid were chosen for cyclization. They were prepared in the usual way from α,α-diphenyl-β-bromopropionyl chloride. During the preparation of the acid chloride it was observed to undergo an interesting decomposition to 1,1-diphenyl-2-bromoethylene, with the evolution of carbon monoxide and hydrogen chloride. The impure acid chloride decomposed even on prolonged heating in vacuum on the water bath. However, the recrystallized substance was considerably more stable; it had to be heated to 180-200° to bring about breakdown:

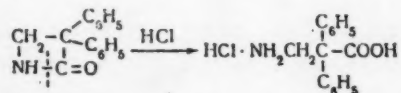


Decarbonylation reactions of acid chlorides have been observed before, but at considerably higher temperature or in the presence of such catalysts as H<sub>2</sub>SO<sub>4</sub> or AlCl<sub>3</sub> [5, 6]. All the α,α-diphenyl-β-bromopropionamides synthesized by us cyclized easily into the corresponding azetidinones-2 (Table 1). In particular, 3,3-diphenylazetidinone-2 (unsubstituted at nitrogen) was obtained in quantitative yield:

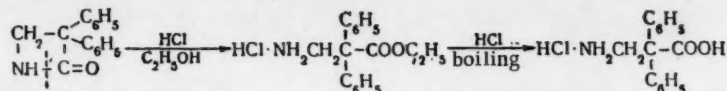


Until recently, all the methods for synthesizing β-lactams were shown to be inapplicable to the synthesis of azetidinones-2, unsubstituted at the nitrogen atom. It was not until 1958 that an azetidinone-2 substituted at position "3" was successfully prepared, starting from an ester or a hydrochloride of β-aminoacyl chloride [7, 8].

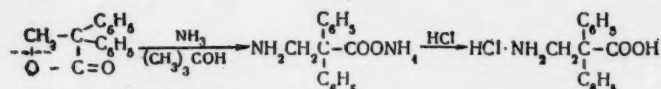
The structure of 3,3-diphenylazetidinone-2 was confirmed by acid hydrolysis when α,α-diphenyl-β-amino-propionic acid separated as its hydrochloride



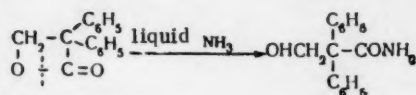
When the lactam is hydrolyzed with ethanolic hydrogen chloride, even in the presence of considerable moisture, the initial product of reaction is the hydrochloride of ethyl  $\alpha,\alpha$ -diphenyl- $\beta$ -aminopropionate, which in its turn can be hydrolyzed with concentrated HCl to the aminoacid hydrochloride.



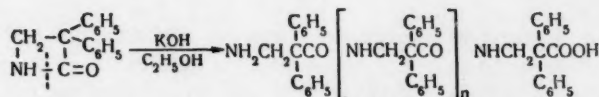
The same  $\beta$ -aminoacid was formed by the action of gaseous ammonia on  $\alpha,\alpha$ -diphenyl- $\beta$ -propiolactone in anhydrous trimethylcarbinol:



$\alpha,\alpha$ -diphenyl- $\beta$ -hydroxypropionamide was obtained by the aminolysis of  $\alpha,\alpha$ -diphenyl- $\beta$ -propiolactone with liquid ammonia:

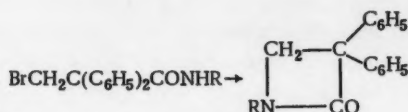


The potassium salt of the polymeric aminoacid is obtained by the action of alcoholic alkali on 3,3-diphenylazetidinone-2.



Apart from the indirect evidence in [9], this is the first experimental confirmation that it is possible to polymerize  $\beta$ -lactams with four-membered rings. We carried out pilot experiments on the polymerization of 3,3-diphenylazetidinone-2 in the presence of traces of metallic sodium and obtained a high melting polyamide which was insoluble in the usual organic solvents but soluble in phenol and cresol. The properties of this polymer are being studied.

TABLE 1. Preparation and Properties of  $\beta$ -Lactams



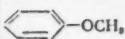

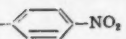
| R  | Reaction conditions               |                      | Yield, % | M. p., °C<br>(from alcohol) | Found, % |      |      | Calculated, % |      |      |
|--|-----------------------------------|----------------------|----------|-----------------------------|----------|------|------|---------------|------|------|
|  | base                              | solvent              |          |                             | C        | H    | N    | C             | H    | N    |
| H  | KNH <sub>2</sub>                  | NH <sub>3</sub> liq. | 95,2     | 168—169                     | 80,75    | 5,95 | 6,58 | 80,71         | 5,83 | 6,97 |
|  | C <sub>2</sub> H <sub>5</sub> ONa | Abs. ethanol         | 94,3     |                             |          |      |      |               |      |      |
|  | KOH                               | "                    | 95,2     |                             |          |      |      |               |      |      |
| C <sub>6</sub> H <sub>5</sub>                      | KNH <sub>2</sub>                  | NH <sub>3</sub> liq. | 98,3     | 168—170                     | 84,15    | 5,66 | 4,94 | 84,26         | 5,66 | 4,35 |
|  | KOH                               | Methylethylketone    | 98,0     |                             |          |      |      |               |      |      |
|  | "                                 | Abs. ethanol         | 94,0     |                             |          |      |      |               |      |      |
| n-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> — | C <sub>2</sub> H <sub>5</sub> ONa | "                    | 90,0     | 148—149                     | 80,02    | 5,66 | 4,45 | 80,24         | 5,59 | 4,25 |
| n-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> —  | C <sub>2</sub> H <sub>5</sub> ONa | "                    | 90,0     | 177—179                     | 73,37    | 4,38 | 8,27 | 73,25         | 4,65 | 8,13 |
| C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> —    | NaSH                              | Alcohol              |          | 140—141                     | 83,86    | 5,88 |      | 84,3          | 6,07 |      |

It was shown previously [2] that the rate of cyclization of  $\beta$ -bromosubstituted carboxylic acid amides was determined to a noticeable degree by the acidity of the initial amide. Therefore, the rate increased on introducing a secondary substituent at the para-position on the benzene ring attached to the nitrogen atom. Measurements of the rate of cyclization of  $\alpha,\alpha$ -diphenyl- $\beta$ -bromopropionamides showed (Table 2) that the type of influence exerted by substituents remained the same as for  $\beta$ -bromohydrocinnamides. However the absolute rate values were considerably

higher for  $\alpha,\alpha$ -diphenyl- $\beta$ -bromopropionamides. Amides unsubstituted at the nitrogen atom cyclized noticeably more slowly than amides substituted at nitrogen.

TABLE 2. Rate of Cyclization of  $\alpha,\alpha$ -diphenyl- $\beta$ -bromopropionamides \*

$$\text{BrCH}_2\text{C}(\text{C}_6\text{H}_5)_2\text{CONHR} \xrightarrow{\text{LiOH}} \begin{array}{c} \text{C}_6\text{H}_5 \\ | \\ \text{CH}_2-\text{C} \\ | \quad | \\ \text{RN}-\text{C}-\text{C} \\ | \\ \text{C}_6\text{H}_5 \end{array}$$

| R                | H                           |  |  |  | R                 | H                           | CH <sub>3</sub> |
|------------------|-----------------------------|---|---|---|-------------------|-----------------------------|-----------------|
| Time, min        | Amide used up, % of initial |   |   |   | Time, min         | Amide used up, % of initial |                 |
| In dioxane at 0° |                             |   |   |   | In ethanol at 35° |                             |                 |
| 2                | —                           | 90,0  | 94,0  | 100   | 5                 | 9,0                         | 26,5            |
| 4                | —                           | 93,2  | 95,2  | —   | 15                | 17,5                        | 36,5            |
| 7                | —                           | 94,5  | 98,0  | —   | 30                | 31,5                        | 48,5            |
| 10               | 0                           | 100   | 100   | —   | 60                | 44,5                        | 77              |

\* Equimolar quantities (equal to 0,01 M/liter) were taken in all experiments.

#### EXPERIMENTAL

**Preparation of  $\alpha,\alpha$ -diphenyl- $\beta$ -bromopropionyl chloride.** To a solution of 20,9 g  $\alpha,\alpha$ -diphenyl- $\beta$ -bromopropionic acid in absolute benzene 14,21 g  $\text{PCl}_5$  was added. The solution was boiled for 1 hr, after which the benzene,  $\text{POCl}_3$  and  $\text{HCl}$  were removed in vacuum at 30–40°. The crystalline residue was washed with a small quantity of water.  $\alpha,\alpha$ -Diphenyl- $\beta$ -bromopropionyl chloride (I) was obtained 19,7 g (89,1%) with m. p. 90–92° (from *n*-octane). Found: C 55,73; H 3,83; Br + Cl 35,89%.  $\text{C}_{15}\text{H}_{12}\text{OBrCl}$ . Calculated: C 55,62; H 3,71; Br + Cl 35,69%.

**Thermal decomposition of  $\alpha,\alpha$ -diphenyl- $\beta$ -bromopropionyl chloride.** The nonrecrystallized acid chloride decomposed with the evolution of gaseous products even on heating on a boiling water bath in vacuum. Filter paper moistened with 5%  $\text{PdCl}_2$  darkened in an atmosphere of the gas evolved (qualitative test for CO). Pure (I) was stable in these conditions. 6,47 g recrystallized (I) was heated at 190–210° until no more gas was evolved. 1,1-Diphenyl-2-bromoethylene was obtained 4,25 g (82,4%) with b. p. 131–134°/7 mm and m. p. 41–42° (from ethanol). A mixed melting point determination with addition of 1,1-diphenyl-2-bromoethylene with m. p. 42–43° gave no melting point depression.

**Preparation of  $\alpha,\alpha$ -diphenyl- $\beta$ -bromopropionamides.** All the amides cited in the present work were made by the method described in previous papers [1, 2], except for the *p*-nitrophenylamide of  $\alpha,\alpha$ -diphenyl- $\beta$ -bromopropionic acid. In those cases in which the initial amine was gaseous, it was passed into the cooled acid chloride solution until the appearance of a weakly alkaline reaction to litmus, and the reaction products were worked up immediately. The properties of the amides are cited in Table 3.

**Preparation of the *p*-nitrophenylamide of  $\alpha,\alpha$ -diphenyl- $\beta$ -bromopropionic acid.** A mixture of 16,2 g (0,05 M)  $\alpha,\alpha$ -diphenyl- $\beta$ -bromopropionyl chloride, 6,9 g (0,05 M) *p*-nitroaniline, 4,8 g (0,05 M) triethylamine, and 200 ml absolute benzene was refluxed for some days. The benzene was then evaporated off in vacuum. The solid residue was washed with water and recrystallized from ethanol. The *p*-nitrophenylamide of  $\alpha,\alpha$ -diphenyl- $\beta$ -bromopropionic acid was obtained with m. p. 118–120°. Found: C 58,91; H 4,02; N 6,47%.  $\text{C}_{21}\text{H}_{17}\text{O}_3\text{N}_2\text{Br}$ . Calculated: C 59,36; H 4,00; N 6,58%.

**Decomposition of 3,3-diphenylazetidinone-2 with concentrated HCl.** 0,5 g of the  $\beta$ -lactam was heated with 20 ml concentrated HCl in a sealed ampoule for 20 hr on a boiling water bath. The hydrochloride of  $\alpha,\alpha$ -diphenyl- $\beta$ -aminopropionic acid separated from the cooled solution as large crystals with m. p. 220–230°. In its properties the substance was completely identical with the hydrochloride obtained by ammonolysis of the  $\beta$ -lactam in trimethylcarbinol.

Properties of the Amides  $\text{BrCH}_2\text{C}(\text{C}_6\text{H}_5)_2\text{CONHR}$ 

| R                                    | M. p., °C<br>(from ethanol) | Yield,<br>% | Found, % |      |      |       | Calculated, % |      |      |       |
|--------------------------------------|-----------------------------|-------------|----------|------|------|-------|---------------|------|------|-------|
|                                      |                             |             | C        | H    | N    | Br    | C             | H    | N    | Br    |
| H                                    | 171—171,5                   | 70          | 58,86    | 4,67 |      |       | 59,21         | 4,60 |      |       |
| $\text{CH}_3$                        | 170—171                     | 85          | 60,29    | 4,88 |      | 25,18 | 60,37         | 5,03 |      | 25,16 |
| $\text{C}_6\text{H}_5$               | 153—154 *                   | 73          |          |      | 3,89 |       |               |      | 3,76 |       |
| $p\text{-C}_6\text{H}_4\text{OCH}_3$ | 108—109                     | 91          | 64,20    | 4,75 |      | 18,84 | 64,37         | 4,87 |      | 19,51 |
| $p\text{-C}_6\text{H}_4\text{NO}_2$  | 118—120                     | 90          | 58,91    | 4,02 | 6,47 |       | 58,91         | 4,00 | 6,58 |       |
| $\text{C}_6\text{H}_5\text{CH}_2$    | 172                         | 95,5        | 67,12    | 5,06 |      | 20,23 | 67,0          | 5,07 |      | 20,30 |

\* From absolute ethanol.

Decomposition of 3,3-diphenylazetidinone-2 with ethanolic HCl. 0.5 g of the  $\beta$ -lactam, 20 ml of saturated ethanolic solution of HCl, and 0.2 ml  $\text{H}_2\text{O}$  were boiled for 4 hr. The alcohol was evaporated in vacuum. The residue — 0.54 g of a solid substance — was completely soluble in water without hydrolysis. It dissolved very well in ethanol. It was not precipitated from ethanolic solution by pyridine. The hydrochloride of ethyl  $\alpha, \alpha$ -diphenyl- $\beta$ -aminopropionate was purified by reprecipitation with ether from a saturated ethanolic solution at room temperature; m. p. 194–196°. Found: Cl 11.85%.  $\text{C}_{17}\text{H}_{20}\text{NO}_2\text{Cl}$ . Calculated: Cl 11.82%.

Hydrolysis of the hydrochloride of ethyl  $\alpha, \alpha$ -diphenyl- $\beta$ -aminopropionic acid. 0.35 g of the ester was boiled under reflux for 16 hr with 15 ml concentrated HCl. On cooling 0.2 g of large crystals, m. p. 218–226°, separated from the solution. By evaporation of the filtrate a further 0.06 g of the same crystals was obtained. A mixed melt of the substance with the hydrochloride of  $\alpha, \alpha$ -diphenyl- $\beta$ -propionic acid from  $\alpha, \alpha$ -diphenyl- $\beta$ -propiolactam gave no depression of the melting point.

Decomposition of  $\alpha, \alpha$ -diphenyl- $\beta$ -propiolactone. For decomposition with liquid ammonia 1.2 g  $\alpha, \alpha$ -diphenyl- $\beta$ -propiolactone was added to 150 ml liquid ammonia. Significant solution of the substance was not observed after prolonged shaking. The suspension was kept for 7 days and then the ammonia was evaporated. The solid residue (1.12 g), which was crystallized first from ethanol and then from nitromethane, was  $\alpha, \alpha$ -diphenyl- $\beta$ -hydroxypropionamide, m. p. 167–168°. It was not soluble in bases or alkalis, but it dissolved well in the common organic solvents. Found: C 74.32; H 5.79%.  $\text{C}_{15}\text{H}_{15}\text{N}_2\text{O}_2$ . Calculated: C 74.68; H 6.12%.

For decomposition with ammonia in trimethylcarbinol 2 g of  $\alpha, \alpha$ -diphenyl- $\beta$ -propiolactone was dissolved in 75 ml anhydrous trimethylcarbinol. Dry ammonia was passed into the solution until a precipitate appeared. The reaction mixture was left overnight. The plentiful colloidal precipitate was boiled with water to decompose the ammonium salt. The solid product for decomposition was treated with excess 2 N HCl and the solution evaporated to dryness on a water bath. The hydrochloride obtained was hydrolyzed rapidly on dissolving in water; on recrystallization from ethanol it partially lost HCl. For purification the substance was dissolved in the minimal quantity of boiling ethanol. To the solution 2–3 drops of pyridine were added. The precipitate was filtered off, washed with ethanol and then with water, and dissolved in 2N HCl. The solution was evaporated to dryness. Glistening crystals of the hydrochloride of  $\alpha, \alpha$ -diphenyl- $\beta$ -aminopropionic acid separated, m. p. 220–230° (decomp.). Found: C 64.68; H 5.79; Cl 12.54%.  $\text{C}_{15}\text{H}_{16}\text{O}_2\text{NCl}$ . Calculated: C 64.80; H 5.77; Cl 12.70%.

Decomposition of 3,3-diphenylazetidinone-2 with potassium hydroxide solution. 1 g 3,3-diphenylazetidinone-2 was dissolved in 25 ml absolute ethanol. 10 ml 0.08 N ethanolic KOH was added to the solution. The mixture was boiled on a water bath for 2 hr. Ethanol was evaporated in vacuum. The solid residue (1.1 g) did not dissolve in water, acids or the common organic solvents, but it dissolved in phenol, tricresol and nitrobenzene. On ignition it left an inorganic residue which was soluble in water and turned phenolphthalein red. Found: C 79.86; H 6.04%.  $\text{C}_{15}\text{H}_{13}\text{ON}$ . Calculated: C 80.72; H 5.83%.

Polymerization of 3,3-diphenylazetidinone-2. 1 g of the  $\beta$ -lactam dried at 100° was placed in an ampoule with the smallest possible lump of metallic sodium in an atmosphere of nitrogen. The ampoule was heated at 200–210° for 20 hr. A solid substance was obtained which did not melt or darken on heating to 320°, and which did not dissolve in the common organic solvents. It dissolved in phenol, p-cresol, and, on heating to 160°, in benzyl alcohol.

Determination of the rate of reaction of  $\alpha, \alpha$ -diphenyl- $\beta$ -bromopropionamides with lithium hydroxide solution. The rate of reaction of the amides of the  $\beta$ -bromosubstituted acids with 0.25 N LiOH solution was determined from the quantity of bromide ion removed. This was done by the method described in detail in a previous paper [2].

## SUMMARY

1. Various amides of  $\alpha,\alpha$ -diphenyl- $\beta$ -bromopropionic acid were prepared, and the effect of substituents on the nitrogen atom on the rate of cyclization to the corresponding azetidinone-2 was investigated.

2. 3,3-Diphenylazetidinone-2 unsaturated at nitrogen was synthesized, and it was shown to be possible to polymerize it to a polyamide.

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# ADDITION REACTIONS OF FLUOROOLEFINS

## PART 14. CONCERTED ADDITION OF HALOGENS AND MERCURY SALTS

I. L. Knunyants, E. Ya. Pervova, and V. V. Tyuleneva

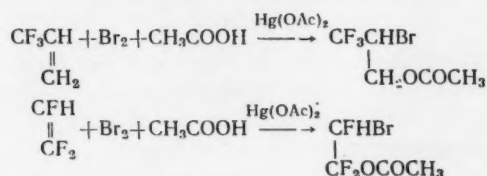
Institute of Heteroorganic Compounds, Academy of Sciences of the USSR

Translated from *Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk*,

No. 1, pp. 88-93, January, 1961

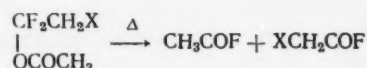
Original article submitted July 16, 1959

In a previous communication it was shown that polyfluoroolefins underwent a concerted reaction with bromine in glacial acetic acid solution in the presence of mercuric acetate to form polyfluorobromoacetoxyparaffins [1].

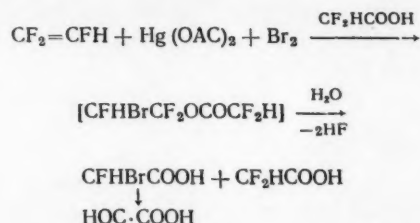


In a continuation of this investigation, trichloroacetic, trifluoroacetic, and difluoroacetic acids were brought into a concerted reaction with bromine and polyfluoroolefins. An analogous reaction was carried out with chlorine in glacial acetic acid solution in the presence of mercuric acetate.

The formulas, physical constants, and analytical results for the new polyfluorohalogenoacylparaffins are cited in the table. The acetate and trihaloacetates of  $\gamma, \gamma, \gamma$ -trifluoro- $\beta$ -bromopropanol are stable compounds which do not decompose on keeping. In contrast to these compounds, the acetates of  $\beta$ -halo- $\alpha, \alpha'$ -difluoroalcohols, which were obtained by the concerted addition of halogens in acetic acid solution with 1,1-difluoroethylene and trifluoroethylene, are unstable and have the characteristics of mixed anhydrides. On heating they decompose with formation of the corresponding haloacetyl halide.

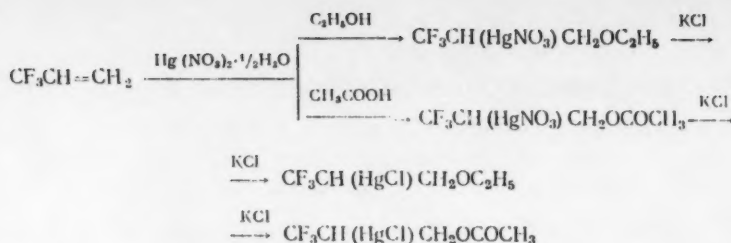


The difluoroacetates of  $\alpha, \alpha$ -difluoroalkanoils are particularly unstable to hydrolysis. They hydrolyze during the preparative process with the formation of halogen substituted acetic acids:

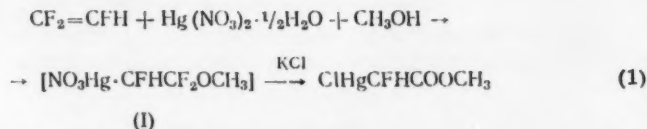


In continuing the investigation of the mechanism of concerted addition of halogens to olefins, it was found that 1,1,1-trifluoropropene and trifluoroethylene, to which mercuric acetate had not been successfully added, easily combined with mercuric nitrate,  $\text{Hg}(\text{NO}_3)_2 \cdot \frac{1}{2}\text{H}_2\text{O}$ , either in ethanolic or glacial or acetic acid solution. The addition products from 1,1,1-trifluoropropene and mercuric nitrate were identified in the form of (1,1,1-trifluoro-3-acetoxypropyl-2)mercuric chloride and (1,1,1-trifluoro-3-ethoxypropyl-2)mercuric chloride.

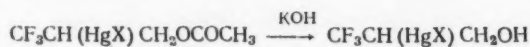
| Fluoroolefins | Polyfluorohalogenoacyl-<br>paraffins | Yield, % | B.p., °C<br>(mm Hg) | Found      |            |       |       |      | Calculated |       |       |       |      |
|---------------|--------------------------------------|----------|---------------------|------------|------------|-------|-------|------|------------|-------|-------|-------|------|
|               |                                      |          |                     | $n_D^{20}$ | $d_4^{20}$ | MR    | C, %  | H, % | F, %       | MR    | C, %  | H, %  | F, % |
| $CF_3CH=CH_2$ | $CF_3CHBrCH_2OCOCCH_3$               | 65       | 82(8)               | 1.4470     | 1.8342     | 49.30 | 18.61 | 1.24 | —          | 49.01 | 17.73 | 0.88  | —    |
|               | $CF_3CHBrCH_2OCOCF_3$                | 53       | 48(15)              | 1.3700     | 1.7692     | 36.31 | 20.70 | 1.57 | —          | 35.55 | 20.76 | 1.37  | —    |
|               | $CF_3CHClCH_2OCOCCH_3$               | 52       | 436                 | 1.3710     | 1.3522     | 31.98 | 31.10 | 3.52 | —          | 32.12 | 31.49 | 3.15  | —    |
| $CF_2=CH_2$   | $CH_2BrCF_2OCOCCH_3$                 | 50       | 63(7)               | 1.4531     | 1.8530     | 44.68 | 15.93 | 0.82 | —          | 45.00 | 15.06 | 0.65  | —    |
|               | $CH_2ClCF_2OCOCCH_3$                 | 43       | 24(11)              | 1.3763     | 1.3512     | 27.00 | 30.65 | 3.20 | —          | 27.19 | 30.28 | 3.15  | —    |
| $CF_2=CFH$    | $CFHBrCF_2OCOCCH_3$                  | 55       | 55(7)               | 1.4330     | 1.880      | 44.87 | 15.00 | 0.61 | —          | 44.69 | 14.79 | 0.307 | —    |
|               | $CFHClCF_2OCOCCH_3$                  | 40       | 54(110)             | 1.3585     | 1.4152     | 27.44 | 27.29 | 2.39 | —          | 27.50 | 27.19 | 2.26  | —    |



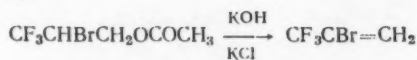
In the same conditions trifluoroethylene formed with ethanolic mercuric nitrate an unstable addition product (I), which on hydrolysis gave an organomercurial derivative of methyl monofluoroacetate



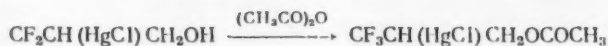
The ability of hydrogen-containing fluoroolefins to add mercuric salts in polar solvents with the formation of mercury derivatives of fluoroolefins raises anew the question of whether organomercury derivatives of fluoroolefins are intermediates in the formation of polyfluorobromoacylparaffins. However, individual products were not successfully isolated from attempted concerted additions of bromine to 1,1,1-trifluoropropene, 1,1-difluoroethylene, and trifluoroethylene in glacial acetic acid in the presence of mercuric nitrate, whereas in the presence of mercuric acetate and sulphate, polyfluorohalogenoacylparaffins were obtained in good yield. Moreover, all attempts to convert (1,1,1-trifluoro-3-acetoxypentyl-2)mercuric nitrate (chloride) into 1,1,1-trifluoro-3-acetoxy-2-bromopropane, and also to convert (1,1,1-trifluoro-acetoxypentyl-2)mercuric acetate into 1,1,1-trifluoro-acetoxy-2-bromoethane by converting  $-HgX$  into bromine led to negative results. The lack of mobility of  $-HgX$  is explained by the neighboring strong electron-acceptor groups. These facts favor the concerted addition mechanism of halogens in polar solvents in the presence of mercuric salts. Many attempts to obtain (1,1,1-trifluoropropenyl-2)mercuric chloride from (1,1,1-trifluoro-3-acetoxypentyl-2)mercuric chloride by treatment with 50% ethanolic potassium hydroxide or by boiling it with solid potassium hydroxide led only to hydrolysis of the ester group



Nevertheless, treatment of 1,1,1-trifluoro-3-acetoxy-2-bromoethane with 60% potassium hydroxide led to the elimination of acetic acid and to the formation of 1,1,1-trifluoro-2-bromo-propene



Negative results were obtained on attempting to dehydrate (1,1,1-trifluoro-3-hydroxypentyl-2)mercuric chloride with phosphorus pentoxide; on pyrolysis 1,1,1-trifluoropropene was formed. On treating (1,1,1-trifluoro-3-hydroxypentyl-2)mercuric chloride with acetic anhydride (1,1,1-trifluoro-3-acetoxypentyl-2)mercuric chloride was obtained



## EXPERIMENTAL

Halogenoacyloxyderivatives of fluoroolefins were prepared by the method described previously [1]. The physical constants and analyses of the compounds obtained are cited in the table.

Interaction of 1,1-difluoroethylene with bromine in difluoroacetic acid. Vinylidene fluoride was passed into a solution of 10 g mercuric acetate in 25 g difluoroacetic acid while 8 g bromine was simultaneously added dropwise. The reaction flask was cooled in ice. At the end of the reaction the precipitated  $\text{HgBr}_2$  was filtered off and washed with a small quantity of ether. The filtrate was diluted with ice water. The organic layer was separated, dissolved in ether, washed with water, and dried over magnesium sulphate. On distillation in vacuum, decomposition occurred and fluoroacetic acid, b. p.  $40^\circ/40$  mm, and bromoacetic acid, b. p.  $90^\circ/40$  mm, m. p.  $49^\circ$  were obtained. Neutralization equivalent: found 134; calculated for  $\text{C}_2\text{H}_3\text{O}_2\text{Br}$  139.

Interaction of trifluoroethylene with bromine in difluoroacetic acid. In an analogous way bromofluoroacetic acid was obtained from trifluoroethylene, bromine, and mercuric acetate in difluoroacetic acid solution. On boiling bromofluoroacetic acid with water, glyoxylic acid was obtained. A mixed melting point of the 2,4-dinitrophenylhydrazone with the 2,4-dinitrophenylhydrazone of authentic glyoxylic acid gave no depression.

Pyrolysis of 1,1,1-difluoroacetoxy-2-bromoethane. On distilling at normal temperatures and  $120^\circ$  1,1,1-difluoroacetoxy-2-bromoethane decomposed into acetyl fluoride with b. p.  $23-25^\circ$ , and bromoacetyl fluoride, with b. p.  $99-100^\circ$ . Neutralization equivalent: found 31.2; calculated for  $\text{C}_2\text{H}_3\text{OF}$  31. An anilide with m. p.  $113^\circ$  was obtained from  $\text{CH}_3\text{COF}$ . A mixed melting point with acetanilide gave no depression. From  $\text{CH}_2\text{BrCOF}$ ; an anilide with m. p.  $132^\circ$  was obtained (literature data, m. p.  $131^\circ$ ). Found: N 6.65%; neutralization equivalent 70.2. Calculated for  $\text{C}_8\text{H}_8\text{OBrN}$ , N 6.45%; neutralization equivalent 70.5.

Pyrolysis of 1,1,1-difluoroacetoxy-2-chloroethane. In an analogous way acetyl fluoride (b. p.  $23^\circ$ ) and chloroacetyl fluoride (b. p.  $77^\circ$ ) were obtained from 1,1,1-difluoroacetoxy-2-chloroethane. Neutralization equivalent: found 48.2; calculated for  $\text{C}_2\text{H}_2\text{OClF}$  47.85. Neutralization equivalent: found 30.9; calculated for  $\text{C}_2\text{H}_3\text{OF}$  31.

Reaction of 1,1,1-trifluoropropene with mercuric nitrate in absolute ethanol. Absolute ethanol (30 ml) and 17 g  $\text{Hg}(\text{NO}_3)_2 \cdot \frac{1}{2}\text{H}_2\text{O}$  were put in a three necked flask, and 1.5 liter trifluoropropene was passed in at room temperature with vigorous stirring. During one hour the whole of the nitrate dissolved; the reaction of mercuric ion with alkali was negative. On standing, a fresh precipitate appeared. On the following day the precipitate was filtered off, and the mother liquor evaporated in a vacuum desiccator. The yield of (1,1,1-trifluoro-3-ethoxypropyl-2)mercuric nitrate was 85%. The salt produced did not melt, dissolved well in organic solvents, and did not dissolve in water. By the usual methods (1,1,1-trifluoro-3-ethoxypropyl-2)mercuric chloride with m. p.  $37-38^\circ$  (from aqueous ethanol) was made from (1,1,1-trifluoro-3-ethoxypropyl-2)mercuric nitrate; this dissolved well in ethanol, ether, benzene, petroleum ether, but was insoluble in water. Found: C 15.49; H 2.40; F 15.07; Cl 8.45%.  $\text{C}_5\text{H}_6\text{OF}_3\text{HgCl}$ . Calculated: C 15.93; H 2.12; F 15.11; Cl 9.42%.

Reaction of 1,1,1-trifluoropropene with mercuric nitrate in glacial acetic acid. In an analogous manner (1,1,1-trifluoro-3-acetoxypropyl-2)mercuric nitrate was obtained in 80% yield from 1,1,1-trifluoropropene and  $\text{Hg}(\text{NO}_3)_2 \cdot \frac{1}{2}\text{H}_2\text{O}$  in glacial acetic acid. Treatment of the product with aqueous potassium chloride gave (1,1,1-trifluoro-3-acetoxypropyl-2)mercuric chloride, m. p.  $95.5^\circ$  (from aqueous ethanol). This substance dissolved well in ether, acetone, ethanol, and benzene, but did not dissolve in water. Found: C 15.17; H 1.49; F 14.87%.  $\text{C}_5\text{H}_6\text{O}_2\text{F}_3\text{ClHg}$ . Calculated: C 15.74; H 1.57; F 14.96%.

Reaction of trifluoroethylene with mercuric nitrate in absolute methanol. Absolute methanol (30 ml) and 5 g  $\text{Hg}(\text{NO}_3)_2 \cdot \frac{1}{2}\text{H}_2\text{O}$  were placed in a flask and trifluoroethylene passed in at room temperature with vigorous stirring. All the nitrate dissolved in 1 hr, and the alkali reaction for mercuric ion became negative. The methanol was evaporated in vacuum at room temperature. The residual oil immediately hydrolyzed with considerable evolution of heat and hydrogen fluoride. In this way rapid crystallization of the reaction mass occurred. The methyl ester of nitratomercurimonofluoroacetic acid was obtained, 4.5 g (83%) with m. p.  $100-103^\circ$  (decomp.). This substance dissolved well in ethanol, water, poorly in benzene, and did not dissolve in ether. By a normal method it was converted into the methyl ester of chloromercurimonofluoroacetic acid with m. p.  $181-182^\circ$  (decomp.) (from absolute ethanol). It dissolved in ethanol and acetone, but did not dissolve in water or ether. Found: C 10.86; H 1.19; F 6.65%. Calculated: C 11.02; H 1.22; F 5.81%.

Reaction of (1,1,1-difluoroacetoxyethyl-2)mercuric acetate with bromine. In a three necked flask 50 ml glacial acetic acid and 15.5 g (0.05 M) mercuric acetate were placed. 1,1-Difluoroethylene was passed in at room

temperature with vigorous stirring. As soon as the alkali reaction for mercuric ion became negative, 8 g (0.05 M) bromine was added and stirring at room temperature was continued for 5 hr. The solution remained strongly colored with bromine. No precipitate of  $\text{HgBr}(\text{OCOCH}_3)$  appeared. On the addition of water the liquid did not separate into layers, thus showing the absence of 1,1,1-difluoroacetoxy-2-bromoethane.

Reaction of (1,1,1-trifluoro-3-acetoxypropyl-2)mercuric nitrate with bromine. In a similar way an experiment was carried out with 1,1,1-trifluoropropene,  $\text{Hg}(\text{NO}_3)_2 \cdot \frac{1}{2} \text{H}_2\text{O}$ , and bromine in glacial acetic acid. Bromine did not react with (1,1,1-trifluoroacetoxypropyl-2)mercuric nitrate at room temperature.

Reaction of 1,1,1-trifluoro-2-bromo-3-acetoxypropane with potassium hydroxide. 32 g 1,1,1-trifluoro-2-bromo-3-acetoxypropane was added with vigorous stirring to a 60% solution of potassium hydroxide heated at 100°. The 1,1,1-trifluoro-2-bromopropene formed was collected in a trap, yield 50%; b. p. 35°;  $n_D^{20}$  1.3409 (according to the literature b. p. 33°;  $n_D^{25}$  1.3503). For identification it was converted to its dibromide;  $\text{CF}_3\text{CBr}_2\text{CH}_2\text{Br}$  was obtained in 80% yield; b. p. 53°/18 mm;  $n_D^{20}$  1.4840 (according to the literature b. p. 79-81°/47 mm,  $n_D^{20}$  1.4831 [2]). Found: C 11.12; H 0.65; Br 71.66; F 17.97%.  $\text{C}_3\text{H}_2\text{Br}_3\text{F}_3$ . Calculated: C 10.77; H 0.59; Br 71.41; F 17.01%.

Preparation of (1,1,1-trifluoro-3-hydroxypropyl-2)mercuric chloride. 4.5 g (1,1,1-trifluoro-3-acetoxypropyl-2)mercuric chloride was shaken with 3.5 ml 50% potassium hydroxide at room temperature. All the solid dissolved when the reaction mixture was heated. The solution was filtered and then dry carbon dioxide and 8 ml 10% sodium chloride solution were added simultaneously. The mixture was extracted three times with ether, and the ethereal extracts dried with magnesium sulphate. An oil was left after evaporation of the ether, and this oil crystallized on standing. The yield of (1,1,1-trifluoro-3-hydroxypropyl-2)mercuric chloride was 80%; m. p. 62-66° (chloroform); it dissolved well in ether, water, ethanol, and benzene, poorly in chloroform, and did not dissolve in petroleum ether. Found: C 10.65; H 1.32%.  $\text{C}_3\text{H}_4\text{OF}_3\text{HgCl}$ . Calculated: C 10.37; H 1.15%.

(1,1,1-Trifluoro-3-hydroxypropyl-2)mercuric bromide, m. p. 65-67°, was also prepared. Found: C 9.95; H 1.38; Hg 51.87%.  $\text{C}_3\text{H}_4\text{OF}_3\text{HgBr}$ . Calculated: C 9.10; H 1.01; Hg 50.90%.

Reaction of (1,1,1-trifluoro-3-hydroxypropyl-2)mercuric chloride with acetic anhydride. 2 g (1,1,1-trifluoro-3-hydroxypropyl-2)mercuric chloride and 15 ml acetic anhydride were heated under reflux for 2 hr. The excess acetic anhydride was evaporated in vacuum. The dry residue was crystallized from aqueous alcohol. The yield of (1,1,1-trifluoro-3-acetoxypropyl-2)mercuric chloride was 60%; m. p. 95°. A mixed melting point with (1,1,1-trifluoro-3-acetoxypropyl-2)mercuric chloride prepared earlier gave no depression.

Pyrolysis of (1,1,1-trifluoro-3-hydroxypropyl-2)mercuric chloride. 30 g (1,1,1-Trifluoro-3-hydroxypropyl-2)mercuric chloride was heated in a Wurtz flask on a Woods metal bath. The flask was connected to a trap cooled to -60°. At a temperature of 130° decomposition began. 6.5 g (75%) 1,1,1-trifluoropropene was obtained which was identified by conversion to its dibromide,  $\text{CF}_3\text{CHBrCH}_2\text{Br}$ , b. p. 114°;  $n_D^{20}$  1.4310 (literature data, b. p. 115°;  $n_D^{25}$  1.4280 [2]).

#### SUMMARY

1. Concerted addition of halogens to polyfluoroolefins in perhalogenated acid solutions have been carried out. A series of new haloacetates of  $\alpha,\alpha$ -difluoro- $\beta$ -bromo(chloro) substituted alcohols has been prepared.
2. Concerted additions of highly dissociated mercuric salts to polyfluoroolefins have been carried out in acetic acid and alcohol to form unsymmetrical organomercury compounds with either hydroxy or acetoxy groups in the polyfluoroinated radical.

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# ON THE CHEMICAL COMPOSITION OF CRACKED GASOLINES FROM NAPHTHENIC RAW MATERIAL

## PART I. COMBINED METHOD OF INVESTIGATION OF THE DETAILED GROUP

### CHEMICAL COMPOSITION OF CRACKED GASOLINES

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The liquid hydrocarbons of petroleum and its conversion products are the most important potential source of raw materials for petrochemical synthesis. In order to increase the resources of monomeric hydrocarbon raw material, systematic investigative work must be done both in the field of the conversion technology of petroleum hydrocarbons and that of their chemistry. The study of the nature of unsaturated hydrocarbons formed in the processes of thermal and catalytic conversion of petroleum distillates merits special attention, since this hydrocarbon group is characterized by increased reactivity.

Our investigations [1-5] and those of foreign authors [6-7] showed that the hydrocarbon composition of gasolines obtained in the thermal and catalytic conversion of petroleum distillates is more complex and varied than the composition and structure of straight-run gasoline hydrocarbons. The variety in the composition and structure of the hydrocarbons obtained depends on several factors. The main factors are the chemical and fractional composition of the original raw material going into cracking, and the conditions of the process. From both the theoretical and practical points of view, it is of substantial interest to study the effect of the chemical composition of the original raw material going into thermal and catalytic cracking on the composition and structure of the hydrocarbons obtained in the indicated processes.

TABLE 1. Characteristics of the Original Gasolines

| Gasoline    | Characteristics |            |               |
|-------------|-----------------|------------|---------------|
|             | $n_D^{20}$      | $d_4^{20}$ | Iodine number |
| Gasoline-12 | 1,4390          | 0,7732     | 61,0          |
| Gasoline-2  | 1,4230          | 0,7505     | 120           |
| Gasoline-11 | 1,4331          | 0,7710     | 131           |

In order to find out the nature of the hydrocarbon components of the cracking products, a reliable method must be developed for investigating both their detailed-group and individual-hydrocarbon composition. The chromatographic method which we developed [3], permits the separation of cracked gasolines into naphthene-paraffin, unsaturated, and aromatic hydrocarbons. In the present article a combined method is described, which includes chromatographic separation of standard fractions (60-175°) of cracked gasoline into hydrocarbon

classes, in combination with hydrodehydrogenation catalysis and the aniline method. This method makes it possible to determine the chemical composition of fractions separately for seven subgroups of saturated and unsaturated hydrocarbons.

### EXPERIMENTAL

In order to develop the method and to investigate the hydrocarbon composition, bulk distillates of three gasoline samples were taken. These samples were obtained in the thermal and catalytic cracking of distillates of choice Surakhany naphthenic petroleum: 1) catalytic-cracking gasoline (B-12) obtained from the kerosine-gas oil fraction (235-360°) over an aluminosilicate catalyst at 460°; 2) thermal-cracking gasoline (B-2) obtained from the petroleum residue (above 360°) at 515° and 38-40° atm pressure; 3) thermal-cracking gasoline (B-11) obtained from the kerosine-gas oil fraction (235-360°) at 515° and 40 atm pressure.

TABLE 2. Characteristics of Gasoline Fractions

| Characteristics of fraction                      | Gasoline-12 |        |         |         |        | Gasoline-2 |         |         |        |        | Gasoline-11 |         |        |        |         |
|--|-------------|--------|---------|---------|--------|------------|---------|---------|--------|--------|-------------|---------|--------|--------|---------|
|  | 60-95       | 95-122 | 122-150 | 150-175 | 60-95  | 95-122     | 122-150 | 150-175 | 60-95  | 95-122 | 122-150     | 150-175 | 60-95  | 95-122 | 122-150 |
| Yield, reckoned on 60-175° gasoline $n_{D}^{20}$ | 28,3        | 20,2   | 24,7    | 26,8    | 20,5   | 23,6       | 31,1    | 24,8    | 25,0   | 25,9   | 26,5        | 22,6    | 25,0   | 25,9   | 26,5    |
| $d_{4}^{20}$                                     | 1,4048      | 1,4439 | 1,4690  | 1,4736  | 1,3989 | 1,4164     | 1,4292  | 1,4361  | 1,4110 | 1,4308 | 1,4387      | 1,4478  | 1,4110 | 1,4308 | 1,4387  |
| Aniline point                                    | 0,7171      | 0,7906 | 0,8274  | 0,8335  | 0,7035 | 0,7410     | 0,7644  | 0,7826  | 0,7276 | 0,7724 | 0,7817      | 0,8006  | 0,7276 | 0,7724 | 0,7817  |
| Iodine number                                    | 38,2        | 14,5   | 4,8     | 9,6     | 41,0   | 41,3       | 43,8    | 47,3    | 25,5   | 24,5   | 30,8        | 37,4    | 25,5   | 24,5   | 30,8    |
| Diene number                                     | 113,6       | 78,6   | 30,5    | 10,0    | 151,8  | 130,4      | 166,0   | 92,0    | 157,2  | 122,4  | 111,3       | 88,0    | 157,2  | 122,4  | 111,3   |
| Molecular weight                                 | —           | —      | —       | —       | 3,8    | 6,0        | 3,8     | —       | 3,7    | 4,3    | 4,3         | —       | 3,7    | 4,3    | 4,3     |
|  | 92,0        | 98,7   | 107,3   | 123     | 92,8   | 107,8      | 120,0   | 136,5   | 100    | 108    | 116,5       | 132,7   | 100    | 108    | 116,5   |

TABLE 3. Group Composition of Narrow Gasoline Fractions

| Characteristics of fraction | Gasoline-12 |        |         |         |        | Gasoline-2 |         |         |        |        | Gasoline-11 |         |        |        |         |
|-----------------------------|-------------|--------|---------|---------|--------|------------|---------|---------|--------|--------|-------------|---------|--------|--------|---------|
|                             | 60-95       | 95-122 | 122-150 | 150-175 | 60-95  | 95-122     | 122-150 | 150-175 | 60-95  | 95-122 | 122-150     | 150-175 | 60-95  | 95-122 | 122-150 |
| 1. Naphthene-paraffins      |             |        |         |         |        |            |         |         |        |        |             |         |        |        |         |
| Yield, wt. %                | 57,2        | 42,3   | 29,1    | 36,3    | 49,3   | 49,8       | 50,7    | 50,5    | 36,9   | 38,8   | 37,4        | 42,5    | 36,9   | 38,8   | 37,4    |
| $n_{D}^{20}$                | 1,3948      | 1,4152 | 1,4259  | 1,4350  | 1,3883 | 1,4030     | 1,4141  | 1,4233  | 1,3920 | 1,4039 | 1,4190      | 1,4229  | 1,3920 | 1,4039 | 1,4190  |
| $d_{4}^{20}$                | 0,7061      | 0,7514 | 0,7705  | 0,7893  | 0,6895 | 0,7197     | 0,7428  | 0,7612  | 0,7005 | 0,7297 | 0,7547      | 0,7775  | 0,7005 | 0,7297 | 0,7547  |
| Aniline point               | 56,6        | 53,8   | 59,0    | 62,4    | 62,1   | 63,7       | 66,1    | 69,1    | 58,3   | 60,0   | 62,4        | 64,5    | 58,3   | 60,0   | 62,4    |
| 2. Unsaturates              |             |        |         |         |        |            |         |         |        |        |             |         |        |        |         |
| Yield, wt. %                | 37,7        | 23,7   | 9,5     | 4,5     | 49,6   | 45,1       | 39,1    | 36,5    | 50,6   | 41,6   | 43,7        | 38,0    | 50,6   | 41,6   | 43,7    |
| $n_{D}^{20}$                | 1,4120      | 1,4375 | 1,4410  | 1,4480  | 1,4085 | 1,4261     | 1,4349  | 1,4403  | 1,4092 | 1,4271 | 1,4342      | 1,4421  | 1,4092 | 1,4271 | 1,4342  |
| $d_{4}^{20}$                | 0,7221      | 0,7900 | 0,7903  | —       | 0,7156 | 0,7558     | 0,7756  | 0,7831  | 0,7209 | 0,7621 | 0,7740      | 0,7894  | 0,7209 | 0,7621 | 0,7740  |
| Aniline point               | 18,5        | 11,0   | 25,9    | —       | 21,5   | 24,0       | 30,0    | 38,0    | —      | —      | —           | —       | —      | —      | —       |
| Iodine number               | 291,8       | 283,6  | 278,0   | 260,0   | 289,0  | 291,0      | 259,0   | 220,0   | 299,0  | 256    | 242         | 213     | 299,0  | 256    | 242     |
| 3. Aromatics                |             |        |         |         |        |            |         |         |        |        |             |         |        |        |         |
| Molecular weight            | 90,8        | 108,2  | 119,0   | 131,0   | 91,6   | 106,4      | 118,6   | 134,0   | 89,5   | 108,0  | 119,5       | 136     | 89,5   | 108,0  | 119,5   |
| Yield, wt. %                | 5,1         | 34,0   | 61,4    | 59,7    | 1,1    | 5,1        | 10,2    | 12,8    | 12,5   | 19,6   | 18,9        | 19,5    | 12,5   | 19,6   | 18,9    |
| $n_{D}^{20}$                | 1,4959      | 1,4960 | 1,4979  | 1,5011  | —      | 1,4900     | 1,4938  | 1,5000  | 0,4983 | 1,4935 | 1,4950      | 1,5011  | 0,4983 | 1,4935 | 1,4950  |
| $d_{4}^{25}$                | 0,8816      | 0,8667 | 0,8668  | 0,8733  | —      | 0,8576     | 0,8612  | 0,8737  | 0,8735 | 0,8641 | 0,8639      | 0,8757  | 0,8735 | 0,8641 | 0,8639  |
| Iodine number               | 23,3        | 5,5    | 5,5     | 12,0    | —      | 35,7       | 27,5    | 27,3    | 13,0   | 7,2    | 17,0        | 35,5    | 13,0   | 7,2    | 17,0    |

TABLE 4. Characteristics of Naphthene-Paraffin Fractions of Gasolines

| Characteristics of fraction  | Gasoline-12                   |                          |                          |                          |                          |                          |                          |                          | Gasoline-2                    |                          |                          |                          |                          |                          |                          |                          | Gasoline-11                   |                          |                          |                          |  |  |  |  |
|--|-------------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|-------------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|-------------------------------|--------------------------|--------------------------|--------------------------|--|--|--|--|
|  | Boiling range of fraction, °C |                          |                          |                          |                          |                          |                          |                          | Boiling range of fraction, °C |                          |                          |                          |                          |                          |                          |                          | Boiling range of fraction, °C |                          |                          |                          |  |  |  |  |
|  | 60—95                         | 95—122                   | 122—150                  | 150—175                  | 60—95                    | 95—122                   | 122—150                  | 150—175                  | 60—95                         | 95—122                   | 122—150                  | 150—175                  | 60—95                    | 95—122                   | 122—150                  | 150—175                  | 60—95                         | 95—122                   | 122—150                  | 150—175                  |  |  |  |  |
| After dehydrogenation:<br>$n_D^{20}$<br>$d_4^{20}$   | 1,3960<br>0,7067<br>55,0      | 1,4328<br>0,7723<br>33,2 | 1,4430<br>0,7906<br>37,7 | 1,4498<br>0,8063<br>44,7 | 1,3914<br>0,6935<br>59,4 | 1,4114<br>0,7296<br>54,2 | 1,4210<br>0,7504<br>58,2 | 1,4290<br>0,7676<br>64,4 | 1,3961<br>0,7055<br>53,3      | 1,4211<br>0,7476<br>44,6 | 1,4308<br>0,7680<br>48,6 | 1,4403<br>0,7893<br>52,0 | 1,3889<br>0,6919<br>61,9 | 1,4000<br>0,7136<br>66,2 | 1,4133<br>0,7414<br>66,7 | 1,4250<br>0,7664<br>68,5 | 1,3889<br>0,6919<br>61,9      | 1,4000<br>0,7136<br>66,2 | 1,4133<br>0,7414<br>66,7 | 1,4250<br>0,7664<br>68,5 |  |  |  |  |
| Aniline point<br>After sulfonation of the dehydrogenation product:<br>$n_D^{20}$<br>$d_4^{20}$ | 1,3924<br>1,7012<br>59,1      | 1,4037<br>0,7364<br>60,3 | 1,4200<br>0,7567<br>64,6 | 1,4309<br>0,7794<br>66,6 | 1,3859<br>0,6884<br>65,0 | 1,3979<br>0,7076<br>67,8 | 1,4098<br>0,7328<br>69,2 | 1,4194<br>0,7697<br>72,0 | 1,3889<br>0,6919<br>61,9      | 1,4000<br>0,7136<br>66,2 | 1,4133<br>0,7414<br>66,7 | 1,4250<br>0,7664<br>68,5 | 1,3889<br>0,6919<br>61,9 | 1,4000<br>0,7136<br>66,2 | 1,4133<br>0,7414<br>66,7 | 1,4250<br>0,7664<br>68,5 | 1,3889<br>0,6919<br>61,9      | 1,4000<br>0,7136<br>66,2 | 1,4133<br>0,7414<br>66,7 | 1,4250<br>0,7664<br>68,5 |  |  |  |  |
| Aniline point  |                               |                          |                          |                          |                          |                          |                          |                          |                               |                          |                          |                          |                          |                          |                          |                          |                               |                          |                          |                          |  |  |  |  |

TABLE 5. Characteristics of Unsaturated Gasoline Fractions

| Characteristics of fraction  | Gasoline-12                   |                          |                          |         |                          |                          |                          |                          | Gasoline-2               |                          |                          |                          |                          |                          |                          |                          | Gasoline-11              |                          |                          |                          |  |  |  |  |
|--|-------------------------------|--------------------------|--------------------------|---------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--|--|--|--|
|  | Boiling range of fraction, °C |                          |                          |         |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |  |  |  |  |
|  | 60—95                         | 95—122                   | 122—150                  | 150—175 | 60—95                    | 95—122                   | 122—150                  | 150—175                  | 60—95                    | 95—122                   | 122—150                  | 150—175                  | 60—95                    | 95—122                   | 122—150                  | 150—175                  |                          |                          |                          |                          |  |  |  |  |
| After hydrogenation of un-saturates:<br>$n_D^{20}$<br>$d_4^{20}$                                 | 1,3997<br>0,6961<br>59,4      | 1,4140<br>0,7082<br>52,2 | 1,4213<br>0,7620<br>59,4 | —       | 1,3901<br>0,6956<br>61,1 | 1,4078<br>0,7312<br>59,4 | 1,4181<br>0,7523<br>63,2 | 1,4260<br>0,7671<br>68,2 | 1,3910<br>0,6984<br>59,7 | 1,4083<br>0,7348<br>59,8 | 1,4180<br>0,7526<br>63,0 | 1,4273<br>0,7719<br>65,7 | 1,3933<br>0,7000<br>57,0 | 1,4199<br>0,7466<br>46,7 | 1,4281<br>0,7639<br>51,6 | 1,4370<br>0,7810<br>54,9 | 1,3884<br>0,6915<br>62,8 | 1,4013<br>0,7151<br>66,2 | 1,4129<br>0,7401<br>67,9 | 1,4218<br>0,7579<br>70,7 |  |  |  |  |
| Aniline point<br>After dehydrogenation of the hydrogenation product:<br>$n_D^{20}$<br>$d_4^{20}$ | 1,3908<br>0,6958<br>58,5      | 1,4200<br>0,7554<br>43,7 | 1,4319<br>0,7716<br>49,6 | —       | 1,3915<br>0,6969<br>60,3 | 1,4132<br>0,7372<br>53,2 | 1,4261<br>0,7610<br>53,5 | 1,4332<br>0,7740<br>59,3 | 1,3933<br>0,7000<br>57,0 | 1,4199<br>0,7466<br>46,7 | 1,4281<br>0,7639<br>51,6 | 1,4370<br>0,7810<br>54,9 | 1,3933<br>0,7000<br>57,0 | 1,4199<br>0,7466<br>46,7 | 1,4281<br>0,7639<br>51,6 | 1,4370<br>0,7810<br>54,9 | 1,3884<br>0,6915<br>62,8 | 1,4013<br>0,7151<br>66,2 | 1,4129<br>0,7401<br>67,9 | 1,4218<br>0,7579<br>70,7 |  |  |  |  |
| Aniline point<br>After sulfonation of the dehydrogenation product:<br>$n_D^{20}$<br>$d_4^{20}$   | 1,3889<br>0,6933<br>60,7      | 1,4090<br>0,7398<br>56,8 | 1,4151<br>0,7492<br>63,9 | —       | 1,3878<br>0,6898<br>63,7 | 1,4023<br>0,7203<br>64,7 | 1,4129<br>0,7409<br>67,6 | 1,4209<br>0,7563<br>71,7 | 1,3884<br>0,6915<br>62,8 | 1,4013<br>0,7151<br>66,2 | 1,4129<br>0,7401<br>67,9 | 1,4218<br>0,7579<br>70,7 | 1,3884<br>0,6915<br>62,8 | 1,4013<br>0,7151<br>66,2 | 1,4129<br>0,7401<br>67,9 | 1,4218<br>0,7579<br>70,7 | 1,3884<br>0,6915<br>62,8 | 1,4013<br>0,7151<br>66,2 | 1,4129<br>0,7401<br>67,9 | 1,4218<br>0,7579<br>70,7 |  |  |  |  |
| Aniline point  |                               |                          |                          |         |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |  |  |  |  |

TABLE 6. Chemical Composition of Naphthene-Paraffin Fractions of Gasolines

| Characteristics of fraction   | Gasoline-12 |        | Gasoline-2                    |         |       |        |         | Gasoline-11 |       |        |         |         |
|---|-------------|--------|-------------------------------|---------|-------|--------|---------|-------------|-------|--------|---------|---------|
|   |             |        | Boiling range of fraction, °C |         |       |        |         |             |       |        |         |         |
|   | 60-95       | 95-122 | 122-150                       | 150-175 | 60-95 | 95-122 | 122-150 | 150-175     | 60-95 | 95-122 | 122-150 | 150-175 |
| Naphthene-paraffins   |             |        |                               |         |       |        |         |             |       |        |         |         |
| Cyclohexanes  | 4,9         | 32,2   | 33,8                          | 28,5    | 6,7   | 16,6   | 14,3    | 10,6        | 10,1  | 25,9   | 21,0    | 23,1    |
| Cyclopentanes   | 31,2        | 31,7   | 25,0                          | 29,0    | 15,5  | 20,9   | 20,0    | 13,3        | 23,0  | 22,2   | 25,0    | 24,5    |
| Paraffins   | 63,9        | 36,1   | 41,2                          | 42,5    | 77,8  | 62,5   | 65,7    | 76,1        | 66,9  | 51,9   | 54,0    | 52,4    |
| After dehydrogenation of the naphthene-paraffin fractions, and sulfonation of the hydrogenation product |             |        |                               |         |       |        |         |             |       |        |         |         |
| Cyclopentanes   | 32,8        | 46,7   | 37,8                          | 40,5    | 16,6  | 25,0   | 22,3    | 14,9        | 25,6  | 29,9   | 31,5    | 31,8    |
| Paraffins   | 67,2        | 53,3   | 62,2                          | 59,5    | 83,4  | 75,0   | 76,7    | 85,1        | 74,4  | 70,1   | 68,5    | 68,2    |

TABLE 7. Chemical Composition of Unsaturated Gasoline Fractions

| Composition of fractions in wt. %   | Gasoline-12 |        | Gasoline-2                    |         |       |        |         | Gasoline-11 |       |        |         |         |
|---|-------------|--------|-------------------------------|---------|-------|--------|---------|-------------|-------|--------|---------|---------|
|   |             |        | Boiling range of fraction, °C |         |       |        |         |             |       |        |         |         |
|   | 60-95       | 95-122 | 122-150                       | 150-175 | 60-95 | 95-122 | 122-150 | 150-175     | 60-95 | 95-122 | 122-150 | 150-175 |
| Unsaturated   |             |        |                               |         |       |        |         |             |       |        |         |         |
| Cyclohexenes  | 2,6         | 16,0   | 17,5                          | —       | 4,1   | 14,0   | 18,3    | 17,4        | 7,0   | 23,4   | 19,9    | 20,5    |
| Cyclopentenes   | 28,0        | 48,0   | 37,0                          | —       | 19,5  | 29,4   | 23,3    | 13,5        | 24,2  | 22,8   | 22,0    | 17,0    |
| Alkenes   | 69,4        | 36,1   | 45,5                          | —       | 76,4  | 56,6   | 58,4    | 69,1        | 71,8  | 53,8   | 58,1    | 62,5    |
| After hydrogenation of the unsaturated fractions, followed by dehydrogenation, sulfonation of the dehydrogenation product |             |        |                               |         |       |        |         |             |       |        |         |         |
| Cyclopentenes   | 28,7        | 57,0   | 40,2                          | —       | 20,3  | 34,2   | 28,5    | 16,3        | 22,8  | 29,8   | 27,5    | 21,1    |
| Alkenes   | 71,3        | 43,0   | 59,8                          | —       | 79,6  | 65,8   | 71,5    | 83,7        | 77,2  | 70,2   | 72,5    | 78,6    |

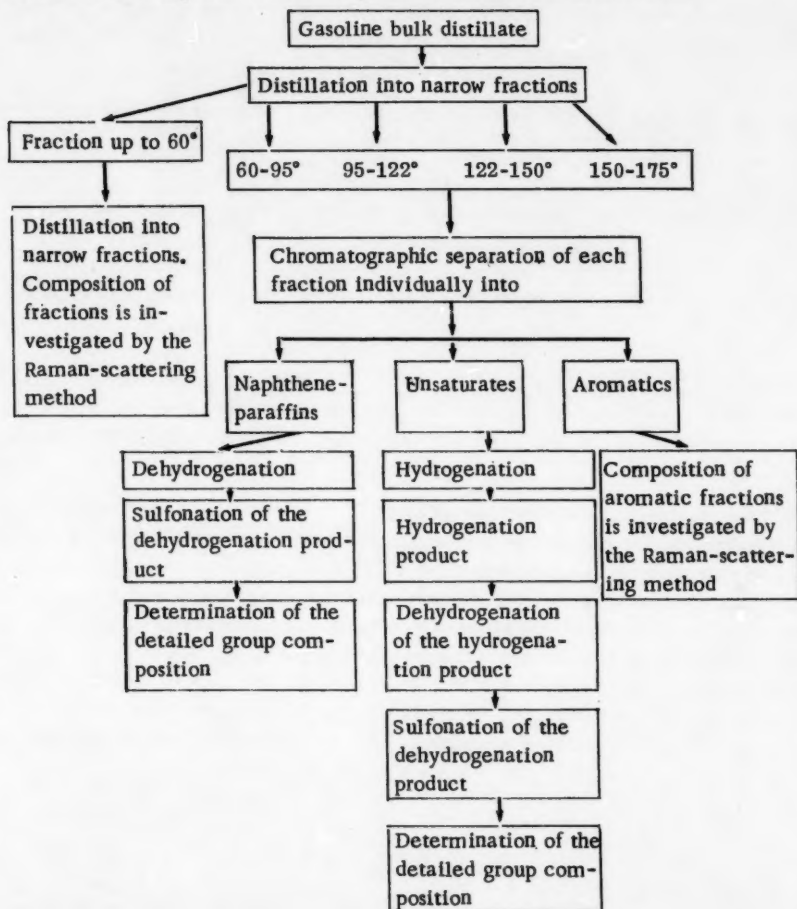
TABLE 8. Detailed Hydrocarbon-Group Composition of Gasolines in wt. % of the Original Fraction

| Hydrocarbons  | Gasoline-12 |        | Gasoline-2                             |         |       |        |         | Gasoline-11 |       |        |         |         |
|---------------|-------------|--------|--|---------|-------|--------|---------|-------------|-------|--------|---------|---------|
|               |             |        | Boiling range of original fraction, °C |         |       |        |         |             |       |        |         |         |
|               | 60-95       | 95-122 | 122-150                                | 150-175 | 60-95 | 95-122 | 122-150 | 150-175     | 60-95 | 95-122 | 122-150 | 150-175 |
| Cyclohexanes  | 2,8         | 13,6   | 9,8                                    | 10,4    | 3,3   | 8,3    | 7,3     | 5,4         | 3,7   | 10,0   | 7,8     | 9,8     |
| Cyclopentanes | 17,8        | 13,4   | 7,3                                    | 10,5    | 7,5   | 10,4   | 10,1    | 6,7         | 8,5   | 8,6    | 9,4     | 10,4    |
| Paraffins     | 36,6        | 15,3   | 12,0                                   | 15,4    | 38,4  | 31,1   | 33,3    | 38,5        | 26,7  | 20,2   | 20,2    | 22,3    |
| Aromatics     | 5,1         | 34,0   | 61,4                                   | 59,7    | 1,1   | 5,1    | 10,2    | 12,8        | 12,5  | 19,6   | 18,9    | 19,5    |
| Cyclohexenes  | 1,0         | 3,8    | 1,7                                    | —       | 2,0   | 6,3    | 7,2     | 6,3         | 3,6   | 9,7    | 8,3     | 7,9     |
| Cyclopentenes | 10,5        | 11,4   | 3,5                                    | 4,0     | 9,7   | 13,3   | 9,1     | 4,9         | 10,7  | 9,5    | 9,2     | 6,6     |
| Alkenes       | 26,2        | 8,5    | 4,3                                    | —       | 37,9  | 25,5   | 22,8    | 25,3        | 36,3  | 22,4   | 24,1    | 24,2    |

The over-all characteristics of the gasoline bulk distillates are given in Table 1. On distillation of the listed gasolines in a 30 plate column the following fractions were taken: Up to 60°, 60-95°, 95-122°, 122-150°, and 150-175°. The characteristics of the fractions obtained are given in Table 2. Each fraction was chromatographically separated into naphthene-paraffin, unsaturated, and aromatic hydrocarbon classes. In order to obtain comparable data and to accumulate a sufficient amount of the corresponding fractions, identical gasoline fractions were chromatographically separated from two to four times. Yields of naphthene-paraffin, unsaturated, and aromatic fractions were determined as the averages of two to three experiments. The over-all yield was 97-98 wt.%. The variance between experiments did not exceed 1%. The content of naphthene-paraffin, unsaturated, and aromatic hydrocarbons in the intermediate fractions (naphthene-paraffin - unsaturated - aromatic), which amounted to 3-5% of the quantity of fraction chromatographed, was determined either by calculation or by repeated separation of the hydrocarbons in a small chromatographic column. The characteristics of the hydrocarbons isolated on chromatographing narrow gasoline fractions are given in Table 3.

Unsaturated hydrocarbons, isolated from each fraction, were hydrogenated at 75-80 atm hydrogen pressure in small autoclaves [8] at 150-200° in the presence of nickel-on-kieselguhr catalyst. A 15-25 ml quantity of the fraction was taken for hydrogenation. The naphthene-paraffin fractions isolated by chromatographing standard fractions, and the products obtained by hydrogenating unsaturated fractions, were separately subjected to analytical dehydrogenation over a catalyst of platinized charcoal with an admixture of iron [9], prepared according to the method described by Musaev and Gal'pern [10]. The fractions were dehydrogenated at 300-302° with a space velocity of 1:1 hr<sup>-1</sup> in the first dehydrogenation, 0.5:1 hr<sup>-1</sup> in the second, and in individual cases 0.3:1 hr<sup>-1</sup> in the third. The catalyzates obtained were characterized, after which they were sulfonated with Katwinkel solution (30 g of P<sub>2</sub>O<sub>5</sub> + 100 ml of H<sub>2</sub>SO<sub>4</sub>).

The separation and investigation of cracked gasolines is shown in the scheme.



Data obtained for naphthene-paraffin fractions are given in Table 4, and those for hydrogenated unsaturated fractions in Table 5.

The content of aromatic hydrocarbons formed from cyclohexanes on dehydrogenation, and the content of pentamethylene hydrocarbons in the dearomatized catalyzate were determined by the aniline method, whereas the content of paraffin hydrocarbons was found by difference. The numerical values of aniline coefficients for calculating aromatic and pentamethylene hydrocarbons were taken from Maslov [11]. The chemical compositions of naphthene-paraffin and hydrogenated unsaturated fractions, after dehydrogenation and sulfonation of the catalyzate, are given in Tables 6 and 7, respectively.

The hydrocarbon-group composition of naphthene-paraffins after dehydrogenation and dearomatization of the catalyzate, and hydrogenated unsaturated fractions after dehydrogenation and dearomatization of the catalyzate, was calculated in the following manner:

1. The percentage of cyclohexane hydrocarbons in the dehydrogenation product

$$Ar_2 = (a - b) \cdot k = A,$$

where  $Ar_2$  denotes aromatic hydrocarbons formed from cyclohexanes on dehydrogenation,  $a$  is the aniline point of the sulfonated dehydrogenation product,  $b$  is the aniline point of the dehydrogenation product, and  $k$  is the aniline coefficient for the aromatic.

2. The percentage of pentamethylene hydrocarbons, reckoned on the sulfonated dehydrogenation product

$$K_n \frac{(T_1 - T_2)}{d} = B,$$

where  $K_n$  is the coefficient for naphthenes,  $T_1$  is the aniline point for paraffins,  $T_2$  is the aniline point of fractions of the sulfonated dehydrogenation product, and  $d$  is the specific gravity of fractions of the sulfonated dehydrogenation product.

3. The percentage of pentamethylene hydrocarbons, reckoned on the original dehydrogenation product

$$\frac{B(100 - A)}{100} = C.$$

4. The percentage of paraffin hydrocarbons, reckoned on the sulfonated dehydrogenation product

$$100 - B = D$$

5. The percentage of paraffin hydrocarbons, reckoned on the original dehydrogenation product

$$100 - (A + C) = E$$

On the basis of A, C, and E the yield of hydrocarbons, reckoned on the original fraction, is calculated in percent: cyclohexanes,  $A.NP/100$ ; cyclopentanes,  $C.NP/100$ ; paraffins,  $E.NP/100$ , where NP is the total yield of naphthene-paraffin hydrocarbons, reckoned on the fraction obtained on chromatographing. The detailed hydrocarbon-group composition of the unsaturated part of the fraction after hydrogenation is similarly calculated.

On the basis of the experimental data obtained (Tables 3-7), the detailed hydrocarbon-group composition of the gasolines was calculated. Summary data on the detailed hydrocarbon-group composition of fractions of the three gasolines, are given in Table 8. As is evident from Table 8, catalytic-cracking gasoline (B-12) differs from thermal-cracking gasolines (B-2 and B-11) by a higher concentration of aromatics and a sharply diminished concentration of unsaturates. Gasoline (B-12) also differs appreciably from gasolines (B-2 and B-11) by an increased concentration (especially in the first two fractions) of cyclopentanes and a diminished concentration of paraffins and alkenes with a very small content of cyclohexenes. In its chemical composition gasoline (B-2) is similar to gasoline (B-11). Gasoline (B-2) differs from gasoline (B-11) mainly in having an increased concentration of paraffins and a sharply diminished concentration of aromatics. The olefin concentration in these two gasolines is very nearly the same.

T. N. Buturlova took part in the work.

#### SUMMARY

1. A combined method has been developed for investigating the detailed hydrocarbon-group composition of cracked gasolines.

2. The proposed method makes it possible to determine the content of hydrocarbons: cyclohexanes, cyclopentanes, paraffins, aromatics, cyclohexenes, cyclopentenes, and alkenes, in standard fractions of thermal- and catalytic-cracking gasolines.

3. The given data show the differences in the chemical composition of the gasolines investigated, due to differences in the chemical composition of the original raw material and the methods of its conversion.

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CONVERSION OF n-HEXANE, METHYLCYCLOPENTANE,  
AND CYCLOHEXANE ON A RHENIUM-ALUMINA CATALYST  
TREATED WITH HYDROGEN SULFIDE

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In 1940 Platonov [1] first communicated the possibility of using rhenium disulfide as a dehydrogenating catalyst for various alcohols and cyclohexane. However, experimental details and method of preparing the catalyst were communicated only for catalytic dehydrogenation of alcohols [2]. In patents of an earlier period the use of rhenium sulfide is indicated as a catalyst in hydrogenation of coal, lignin, asphalt [3], and destructive hydrogenation of oils and other carbon-containing compounds [4]. Broadbent and co-workers [5] carried out comparative evaluation of the catalytic properties of  $\text{Re}_2\text{S}_7$ ,  $\text{ReS}_2$ ,  $\text{MoS}_2$ , and  $\text{CoS}$  in liquid-phase hydrogenation of styrene, phenylacetylene, cyclohexene, benzene, and naphthalene. The authors established that  $\text{Re}_2\text{S}_7$  in these reactions is a more active catalyst than molybdenum and cobalt sulfides.

In our previous work [6] we investigated the catalytic properties of a series of rhenium-alumina catalysts in the conversion of cyclohexane, methylcyclopentane, and n-hexane. In this regard, it was shown possible to dehydrogenate cyclohexane with a high degree of conversion into benzene. The other two hydrocarbons remained either practically unchanged or underwent hydrocracking with formation of hydrocarbons of lower molecular weight than the initial ones.

It was of interest to us to investigate the catalytic properties of a rhenium-alumina catalyst treated with hydrogen sulfide in connection with the conversion of cyclohexane, methylcyclopentane, and n-hexane, i.e., those hydrocarbons which were used in the study of the catalytic properties of rhenium-alumina catalysts [6]. The investigations carried out showed a 20% rhenium-alumina catalyst treated with hydrogen sulfide is more active and stable in dehydrogenation of cyclohexane, dehydroisomerization of methylcyclopentane and dehydrocyclization of n-hexane in benzene than the rhenium-alumina catalysts investigated by us previously [6]. Thus, at 500-510°, 5 atm. hydrogen pressure and ratio of hydrogen to hydrocarbon equal to 5:1, from cyclohexane it is possible to obtain up to 76% of benzene. In the methylcyclopentane catalyzate in the first few hours of the process, benzene content was over 52%. Under the same conditions, n-hexane undergoes marked hydrocracking with formation of hydrocarbons of composition  $\text{C}_1\text{-C}_5$ , in the catalyzate, however, aromatic hydrocarbon content amounts to 10%.

#### EXPERIMENTAL

Metallic rhenium was dissolved in 12%  $\text{HNO}_3$  by boiling on a water bath. Aluminum oxide (commercial) was first calcined in a muffle at 500° for 5 hr as cylinders of size 5 x 5 mm and then saturated with rhenic acid. Rhenium content of the catalyst amounted to 20%. The catalyst was dried off in a drying chamber at 130° for 3-4 hr and treated with hydrogen sulfide in the manner described by us previously for a palladium-alumina catalyst [7].

Experiments were carried out in apparatus of recirculating type [8] at 500-510°, hydrogen pressure 5 atm; hydrocarbon flow rate amounted to 1.0  $\text{hr}^{-1}$  and molar ratio of hydrogen to hydrocarbon ( $\text{H}_2$ :HC) was equal to 5:1. The initial hydrocarbons were passed over the catalyst for 1 hr (the preexperimental period); during this time the rate of flow, temperature, pressure, and ratio  $\text{H}_2$ :HC were established. After the preexperimental period, the experiment was carried out, lasting 2-3 hr. 30 ml of catalyst was placed in the apparatus, a fresh amount of catalyst being used for each hydrocarbon.

Catalyzate analysis was carried out by chromatography, using the method developed in our laboratory [9]. As an illustration of the complete separation of hydrocarbons by this method, in Fig. 1, the n-hexane catalyzate chromatogram is presented. Gaseous products were analyzed on a chromatogram.

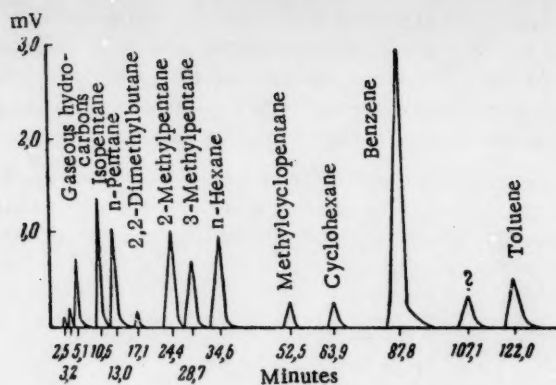


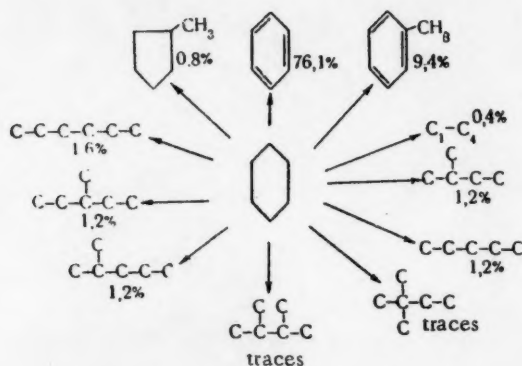
Fig. 1.

n-Hexane used in the investigation had: b. p. 68.5° (754 mm),  $n_D^{20}$  1.3750 and  $d_4^{20}$  0.6599. Methylcyclopentane was obtained by dehydration and isomerization of cyclohexanol over  $Al_2O_3$  at 450°, subsequent hydrogenation of the unsaturated mixture in an autoclave over Raney nickel, and distillation on a column of 80 theoretical plates effectiveness. The hydrocarbon obtained had: b. p. 71.8° (752 mm),  $n_D^{20}$  1.4090 and  $d_4^{20}$  0.7487. Cyclohexane was characterized by b. p. 80.8° (756 mm),  $n_D^{20}$  1.4262 and  $d_4^{20}$  0.7782.

Properties of Catalyzates of Cyclohexane, Methylcyclopentane, and n-Hexane obtained on a Rhenium-Alumina Catalyst treated with Hydrogen Sulfide (500-510°, 5 atm,  $\nu = 1.0 \text{ hr}^{-1}$ , and  $H_2 : HC = 5$ )

| Hydrocarbons       | Yield of catalyzate, % | Degree of conversion, % | Properties |            |
|--------------------|------------------------|-------------------------|------------|------------|
|                    |                        |                         | $n_D^{20}$ | $d_4^{20}$ |
| Cyclohexane        | 98                     | 96.5                    | 1.4800     | 0.8405     |
| Methylcyclopentane | 99                     | 92.9                    | 1.4310     | 0.7550     |
| n-Hexane           | 25                     | 22.0                    | 1.4275     | 0.7365     |

The results obtained on catalysis of cyclohexane, methylcyclopentane, and n-hexane are given in the table and represented by schemes 1-3.

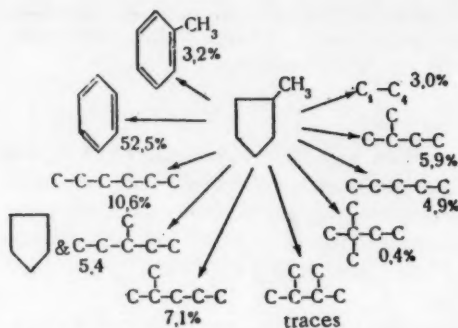


Scheme 1. Conversion of cyclohexane.

As seen from the table and scheme 1, cyclohexane underwent various conversions to the extent of 96.5%. The basic reaction on catalysis of cyclohexane was its dehydrogenation to benzene (76.1%). The presence of methylcyclopentane (0.8%) in the catalyzate is evidence of the occurrence of ring contraction. The presence of 2- and

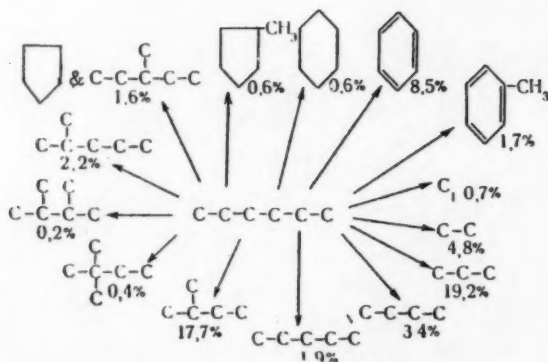
3-methylpentane and also of n-hexane in the catalyzate is explained by hydrogenolysis of the methylcyclopentane formed. Toluene formation (9.4%) can be explained by alkylation of benzene by methylene radicals arising under the conditions of the experiment, as a result of methane rupture of cyclanes, this taking place in the works [6, 10]. It should be noted that despite the high temperature at which the experiment was carried out, yield of liquid catalyzate amounted to 98-99%, and gaseous catalysis products contained mainly hydrogen.

It should be noted that the catalyst in question, after 18 hr operation under the conditions selected, suffered practically no loss of original activity, this not being observed in the case of a rhenium-alumina catalyst. Moreover, treatment of the rhenium-alumina catalyst with hydrogen sulfide led to an increase in its stability double that of the stability of a rhenium-alumina catalyst.



Scheme 2. Conversion of methylcyclopentane.

From an examination of the catalysis products of methylcyclopentane it is seen that the latter undergoes various conversions to the extent of 93%. It is interesting to note the formation in the catalyzate of considerable quantities of benzene (52.5%) and toluene (3.2%), in contrast to the results obtained for the rhenium-alumina catalyst, on which no occurrence of hydroisomerization with formation of aromatic hydrocarbons was observed. In the catalyzate were also found hydrogenolysis products of methylcyclopentane - 2-methylpentane (7.1%), 3-methylpentane (5.4%), and n-hexane (10.6%), and also of hydrocracking - n-pentane (4.9%) and isopentane (5.9%). As in the case of cyclohexane, on catalysis of methylcyclopentane on the catalyst described, a very small amount of gasification was observed (1-2%).



Scheme 3. Conversion of n-hexane.

In catalysis of n-hexane on a rhenium-alumina catalyst treated with hydrogen sulfide, considerable gasification was observed (~75%). Thus, if yield of liquid catalyzate of cyclohexane and methylcyclopentane under the chosen catalysis conditions amounted to 98-99%, then in the case of n-hexane it amounted in all to only 20-25%. However, in the liquid catalysis products, in contrast to the results obtained on a rhenium-alumina catalyst, 10% of aromatic hydrocarbons was observed. On a rhenium-sulfide-alumina catalysts n-hexane conversion proceeded in a very variable manner (scheme 3), and in the catalysis products ten hydrocarbons were found. In the catalyzate was an

obscure hydrocarbon ( $\sim 1\%$ ), occurring on the chromatogram between benzene and toluene (see Fig. 1). In the gaseous portion were observed:  $0.8\% \text{H}_2$ ,  $1.0\% \text{CH}_4$ ,  $6.3\% \text{C}_2\text{H}_6$ ,  $25.5\% \text{C}_3\text{H}_8$ ,  $45.4\% \text{C}_4\text{H}_{10}$ , and  $21.0\% i\text{-C}_5\text{H}_{12}$ .

If the data obtained is compared with that for a rhenium-alumina catalyst [6], it is seen that in the presence of the latter, even at a lower catalysis temperature ( $400^\circ$ ), considerable n-hexane hydrocracking occurs ( $\sim 60\%$ ), no aromatic hydrocarbons being observed in the catalysis products. Consequently, on a rhenium-alumina catalyst treated with hydrogen sulfide, besides dehydrogenation of cyclohexane and dehydroisomerization of methylcyclopentane, n-hexane dehydrocyclization occurs.

#### SUMMARY

1. A study was made of the catalytic properties of a 20% rhenium-alumina catalyst, treated with hydrogen sulfide, in connection with the conversion of cyclohexane, methylcyclopentane, and n-hexane at  $500\text{--}510^\circ$ , 5 atm, pressure of hydrogen,  $\nu = 1.0 \text{ hr}^{-1}$ , and  $\text{H}_2 : \text{HC} = 5$ .

2. The rhenium-sulfide-alumina catalyst promoted the reactions: dehydrogenation of cyclohexane, dehydroisomerization of methylcyclopentane, and dehydrocyclization of n-hexane with formation of benzene, and proved to be more active and stable in the above-mentioned reactions than a rhenium-alumina catalyst.

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# REFORMATION OF GASOLINE ON A RHENIUM-ALUMINA CATALYST TREATED WITH HYDROGEN SULFIDE, WITH THE OBJECT OF IMPROVING ITS OCTANE CHARACTERISTICS

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By investigating the catalytic properties of five rhenium-alumina catalysts [1] we have shown that aromatic hydrocarbons are formed on these catalysts only at the expense of cyclohexane dehydrogenation. Methylcyclopentane and n-hexane under the catalysis conditions chosen undergo chiefly hydrogenolysis and hydrocracking. By studying the conversion of cyclohexane, methylcyclopentane, and n-hexane on a rhenium-alumina catalyst treated with hydrogen chloride [2], we established that aromatic hydrocarbons are formed from all three hydrocarbons. On this catalyst, hydrogenolysis, contraction of a six-membered ring into a five-membered, and other reactions were observed.

It was of interest to investigate the above-mentioned catalyst under conditions where straight-distilled gasoline was reformed with a view to increasing its octane characteristics. In the literature there is only one patent [3] in which is indicated the use of a rhenium-alumina catalyst for reformation of gasoline. Thus, in reformation on this catalyst, the method of preparation of which is not indicated, at 475-500° and 50 atm, pressure of the fraction 100-180° with octane number 53, and containing 14% of aromatic hydrocarbons, a catalyzate was obtained with octane number 71 and aromatic hydrocarbon content 49%.

## EXPERIMENTAL

A 20% rhenium-alumina catalyst treated with hydrogen sulfide was prepared by the method described by us previously [2]. For gasoline reformation, 60 ml of catalyst was placed in the reactor.

Experiments were carried on in an apparatus of recirculating type [4] at 500-510°, 5 atm, hydrogen pressure, flow-rate 1.0 hr<sup>-1</sup>, molecular ratio of hydrogen to gasoline equal to 5:1.

Specific gravity of catalyzate, refractive index, and aromatic hydrocarbon content were determined by the sulfuric acid method, and of sulfur compounds - by the lamp method. Both in the original gasoline and in two catalyzate samples, octane numbers also were determined by the motor and the research method with and without TEL.\*

The gasoline used in the investigation was obtained from the Lyuberets plant and was characterized thus:  $n_D^{20}$  1.4170,  $d_4^{20}$  0.7307; aromatic hydrocarbon content amounted to 10%, and sulfur compounds to 0.056%. The gasoline distilled in the range 38.5-196° at 756 mm, octane number (o.n.) by the motor method was equal to 47.2, and with 1.0 ml/kg TEL was 62.5; o.n. by the research method was 47.8.

Properties of catalyzates obtained as a result of petroleum reformation under the conditions indicated after the first 17 hr operation of the catalyst and after 108 hr are given in the table. In the same table are shown the properties of the initial gasoline. In addition, the octane characteristics are given there of both the initial gasoline and of the catalyzates.

As a result of reforming, aromatic hydrocarbon content after the first 17 hr operation of the catalyst increased to 47%, i.e., increase amounted to 37%. Catalyst activity then gradually fell, and after 85 hr operation aromatic hydrocarbon content amounted to a total of 12%. The exhausted catalyst was regenerated at 400° for 5 hr with nitrogen containing 2.5-3% oxygen. After regeneration, the catalyst was heated in a current of hydrogen at 500° for 3 hr.

\*Octane numbers of the initial gasoline and of the catalyzates were determined at the All-Union Scientific-Research Institute of the Petroleum Industry.

In this manner, the regenerated catalyst regained its original activity completely and worked for a further 23 hr. An average catalyzate sample after 108 hr operation of the catalyst contained 32% of aromatic hydrocarbons. Content of sulfur compounds in catalyzates in the first period of catalyst operation (17 hr) fell to zero, and in the second period (108 hr) decreased three-fold compared with the initial gasoline. Boiling range of the catalyzates did not alter appreciably compared with the boiling range of the initial gasoline. Attention is drawn to the considerable increase in octane numbers of the catalyzates. Thus, when the octane number of the initial gasoline without TEL by the motor method was 47.2, the octane number of the catalyzate (after 17 hr) was equal to 79, i.e., it increased by 31.8 points. The same characteristic determined by the research method equalled 47.8 (initial gasoline), 87.2 (catalyzate after 17 hr), and 71.0 (catalyzate after 108 hr), this amounting to an increase of 39.4 and 23.2 points respectively, compared with the initial gasoline. The data obtained pointed to the possibility of using rhenium catalysts to improve the octane characteristic of low-grade gasolines.

Characteristics of the Initial Gasoline and the Catalyzates Obtained on Its Reformation (500-510°;  $p = 5$  atm,  $\nu = 1$  hr<sup>-1</sup>, and  $H_2 : HC = 5$ )

| Properties                           | Initial gasoline | Catalyst No. 1<br>(after 17 hr<br>operation of<br>catalyst) | Catalyst No. 2<br>(after 108 hr<br>operation of<br>catalyst) |
|--------------------------------------|------------------|---|--|
| Refractive index $n_D^{20}$          | 1.4145           | 1.4390  | 1.4205   |
| Specific gravity $d_4^{20}$          | 0.7307           | 0.7453  | 0.7331   |
| Aromatic hydrocarbon content, vol. % | 10.0             | 47.0  | 32.0   |
| Sulfur compound content, wt. %       | 0.056            | Nil   | 0.019  |
| Engler distillation, °C              | 38.5-196         | 39.5-212  | 44-20  |
| Commencement of boiling              | 38.5             | 39.5  | 44.0   |
| 10%                                  | 70.0             | 66.5  | 75.5   |
| 50%                                  | 128.5            | 124.5   | 125.0  |
| 90%                                  | 183.0            | 184.5   | 178.0  |
| End of boiling                       | 196.0            | 212.0   | 204.0  |
| Octane number                        |                  |   |  |
| by motor method without TEL          | 47.2             | 79.0  | —  |
| by motor method with TEL             | 62.5             | 84.6  | —  |
| by research method without TEL       | 47.8             | 87.2  | 71.0   |
| by research method with TEL          | —                | —   | 80.0   |

#### SUMMARY

1. The catalytic properties were investigated of a 20% rhenium-alumina catalyst treated with hydrogen sulfide in reforming straight-distilled gasoline at 500-510°; 5 atm. hydrogen pressure;  $\nu = 1.0$  hr<sup>-1</sup>, and  $H_2 : HC = 5$ .

2. Under these conditions, catalyzates can be obtained with aromatic hydrocarbon content ranging from 32 to 47%, octane number without TEL increasing from 47.8 for the initial gasoline to 71 and 87.2 respectively.

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DETERMINATION OF THE INDIVIDUAL HYDROCARBON  
CONTENT OF TATAR PETROLEUMS

COMMUNICATION 4. LIGROIN FROM PETROLEUM OF THE ROMASHKIN DEPOSITS

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In previous communications, data has been presented on the investigation of the individual hydrocarbon content of gasolines from Tatar petroleum distilling up to 150° [1]. These works have been carried a stage further by detailed study of the higher-boiling fraction — ligroin (150-200°).

EXPERIMENTAL

As the basis of the method of investigation are presented the generally accepted means of petroleum separation over a wide fraction, chromatographic separation of aromatic hydrocarbons from naphtheno-paraffin ones with subsequent analytical dehydrogenation of the latter on an iron-platinum catalyst and repeated chromatography of the catalyzates. The general scheme of investigation is shown in Fig. 1.

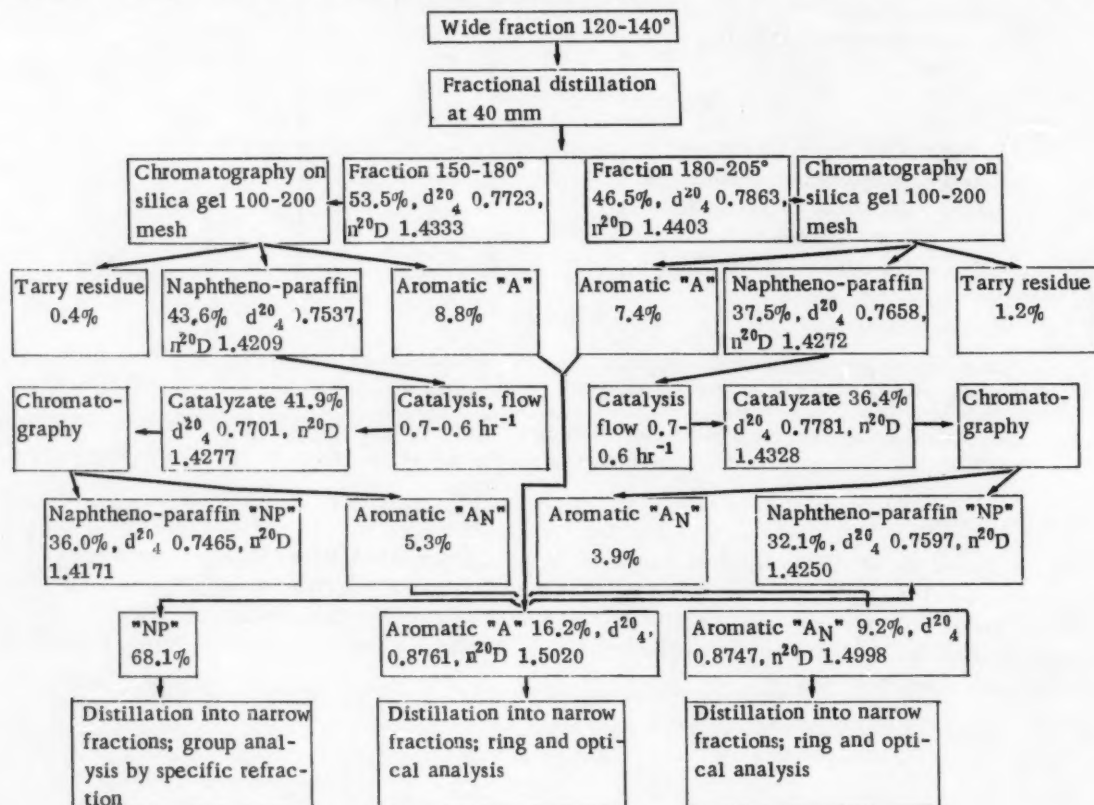


Fig. 1. General scheme of the investigation.

We considered that catalytic dehydrogenation of the fraction 150-180° would proceed more readily than that of the subsequent fraction 180-205°. However, it turned out that both fractions were dehydrogenated with the same difficulty, as a result of fall in catalyst activity. Thus, it was thought undesirable to separate the ligroin into two fractions and the number of further steps in the scheme could be curtailed.

TABLE 1

| Fraction | Boiling ranges, °C | Content in ligroin, % | $d_4^{20}$ | $n_D^{20}$ | $R_A$ | $R_N$ |
|----------|--------------------|-----------------------|------------|------------|-------|-------|
| I        | 159 —163           | 2,0                   | 0,8605     | 1,4939     | 0,94  | 0,02  |
| II       | 163 —171           | 3,1                   | 0,8727     | 1,5010     | 1,00  | 0,05  |
| III      | 171 —174           | 1,1                   | 0,8762     | 1,5039     | 1,00  | 0,09  |
| IV       | 174 —176,5         | 0,7                   | 0,8859     | 1,5040     | 0,99  | 0,20  |
| V        | 176,5—179          | 0,5                   | 0,8809     | 1,5012     | 1,00  | 0,14  |
| VI       | 179 —182,5         | 0,7                   | 0,8706     | 1,4987     | 0,96  | 0,10  |
| VII      | 182,5—185,5        | 1,0                   | 0,8679     | 1,4968     | 0,97  | 0,06  |
| VIII     | 185,5—191          | 1,2                   | 0,8713     | 1,4991     | 0,97  | 0,09  |
| IX       | 191 —195           | 0,8                   | 0,8743     | 1,5008     | 0,98  | 0,12  |
| X        | 195 —200           | 1,5                   | 0,8793     | 1,5051     | 1,00  | 0,13  |
|          | Residue            | 2,9                   |            |            |       |       |
|          | Losses             | 0,7                   |            |            |       |       |
| Total    |                    | 16,2                  |            |            |       |       |

TABLE 2

| Hydrocarbon             | Content in ligroin, % | Hydrocarbon                 | Content in ligroin, % |
|-------------------------|-----------------------|-----------------------------|-----------------------|
| n-Propylbenzene         | 0,4                   | 1-Methyl-3-isopropylbenzene | 0,18                  |
| 1-Methyl-2-ethylbenzene | 0,31                  | 1-Methyl-4-isopropylbenzene | 0,21                  |
| 1-Methyl-3-ethylbenzene | 0,95                  | 1-Methyl-4-propylbenzene    | 0,22                  |
| 1-Methyl-4-ethylbenzene | 0,6                   | 1,2-Dimethyl-4-ethylbenzene | 0,44                  |
| 1,2,3-Trimethylbenzene  | 1,53                  | 1,3-Dimethyl-2-ethylbenzene | 0,12                  |
| 1,2,4-Trimethylbenzene  | 2,83                  | 1,4-Dimethyl-2-ethylbenzene | 0,12                  |
| 1,3,5-Trimethylbenzene  | 0,51                  | 1,3-Dimethyl-5-ethylbenzene | 0,29                  |
| Isobutylbenzene         | 0,08                  | Indan                       | Possibly              |
| sec-Butylbenzene        | 0,09                  | Total                       | 0,37                  |
| n-Butylbenzene          | 0,49                  | Not interpreted             | 3,23                  |

Aromatic and naphtheno-paraffin hydrocarbon content in the ligroin amounted to 16.2 and 81.1%, respectively. The tarry residue obtained by chromatography on a silica gel apparently consisted of a mixture of sulfurous and aromatic hydrocarbons. Hexamethylene hydrocarbon content in the fraction 150-180° was greater than in the subsequent fraction. Total cyclohexane content amounted to ~ 9.6% (9.2 · 1.05).

The aromatic ("A" and "A<sub>N</sub>") and naphtheno-paraffin "NP" hydrocarbons isolated distilled into narrow fractions; their physicochemical constants were determined. Individual aromatic hydrocarbon content in the narrow fractions was determined by the method of combined diffusion of light in an ICP-51 apparatus, and computation of naphthenic and aromatic rings also carried out by specific dispersion [2]. In the naphtheno-paraffin hydrocarbons "NP" group composition was determined for the narrow fractions by specific refraction. Properties of the narrow fractions of aromatic "A" are shown in Table 1.

From Table 1 it is seen that the aromatic hydrocarbons consisted mainly of benzene homologs, but in fractions IV, V, IX, and X indan and its homologs appeared. The composition of the aromatic hydrocarbons determined by optical analysis is shown in Table 2.

The data in Table 2 shows that C<sub>9</sub> alkylbenzenes occur in 7 isomeric forms, the trimethylbenzene content being twice as great as that of the other C<sub>9</sub> hydrocarbons. Ratio of 1-methyl-3-ethylbenzene:1-methyl-4-ethylbenzene:1-methyl-2-ethylbenzene is ~3:2:1. Comparison of the data obtained with that in the literature [3]

shows the proportions of methylethylbenzene isomers in Romashkin ligroin reach approximate equilibrium conditions at a temperature of 455°, such regularity not being observed for other the C<sub>9</sub> hydrocarbons. 1,2,4-Trimethylbenzene is the most widely occurring of the trimethylbenzenes in the ligroin, less 1,2,3-trimethylbenzene being present. It is interesting to note that C<sub>10</sub> dialkylbenzenes having the alkyl groups in the 1,2-position were not observed (1-methyl-2-propylbenzene, 1-methyl-2-isopropylbenzene, 1,2-diethylbenzene).

Properties of the narrow fractions of aromatic "A<sub>N</sub>" (dehydrogenated cyclohexanes) are shown in Table 3.

TABLE 3

| Fraction | Boiling ranges, °C | Content in ligroin, % | $d_4^{20}$ | $n_D^{20}$ | $R_A$ | $R_N$ |
|----------|--------------------|-----------------------|------------|------------|-------|-------|
| I        | 150 —160           | 1,0                   | 0,8582     | 1,4898     | 0,99  | —     |
| II       | 160 —171           | 0,9                   | 0,8658     | 1,4930     | 0,98  | 0,07  |
| III      | 171 —174           | 0,3                   | 0,8697     | 1,4950     | 0,95  | 0,11  |
| IV       | 174 —179           | 0,6                   | 0,8705     | 1,4960     | 0,96  | 0,07  |
| V        | 179 —182,5         | 0,8                   | 0,8668     | 1,4938     | 0,95  | 0,05  |
| VI       | 182,5 —185,5       | 1,1                   | 0,8646     | 1,4930     | 0,96  | 0,11  |
| VII      | 185,5 —190         | 0,6                   | 0,8704     | 1,4948     | 0,98  | 0,03  |
| VIII     | 190 —196           | 0,6                   | 0,8669     | 1,4936     | 0,98  | 0,10  |
| IX       | 196 —205           | 1,5                   | 0,8733     | 1,4971     | 0,98  | —     |
|          | Residue            | 1,5                   |            |            |       |       |
|          | Losses             | 0,3                   |            |            |       |       |
|          | Total              | 9,2                   |            |            |       |       |

TABLE 4

| Aromatic hydrocarbon        | Content in ligroin, % | Naphthene corresponding to it   | Content in ligroin, % |
|-----------------------------|-----------------------|---------------------------------|-----------------------|
| Isopropylbenzene            | 0,30                  | Isopropylcyclohexane            | 0,32                  |
| n-Propylbenzene             | 0,91                  | n-Propylcyclohexane             | 0,95                  |
| 1-Methyl-2-ethylbenzene     | 0,09                  | 1-Methyl-2-ethylcyclohexane     | 0,09                  |
| 1-Methyl-3-ethylbenzene     | 0,24                  | 1-Methyl-3-ethylcyclohexane     | 0,25                  |
| 1-Methyl-4-ethylbenzene     | 0,28                  | 1-Methyl-4-ethylcyclohexane     | 0,29                  |
| 1,2,3-Trimethylbenzene      | 0,43                  | 1,2,3-Trimethylcyclohexane      | 0,45                  |
| 1,2,4-Trimethylbenzene      | 0,13                  | 1,2,4-Trimethylcyclohexane      | 0,14                  |
| Isobutylbenzene             | 0,23                  | Isobutylcyclohexane             | 0,24                  |
| n-Butylbenzene              | 0,36                  | n-Butylcyclohexane              | 0,38                  |
| 1-Methyl-3-isopropylbenzene | 0,22                  | 1-Methyl-3-isopropylcyclohexane | 0,23                  |
| 1-Methyl-4-isopropylbenzene | 0,09                  | 1-Methyl-4-isopropylcyclohexane | 0,09                  |
| 1-Methyl-4-propylbenzene    | 0,40                  | 1-Methyl-4-propylcyclohexane    | 0,42                  |
| 1,2-Dimethyl-4-ethylbenzene | 0,12                  | 1,2-Dimethyl-4-ethylcyclohexane | 0,12                  |
| 1,3-Dimethyl-2-ethylbenzene | 0,06                  | 1,3-Dimethyl-2-ethylcyclohexane | 0,06                  |
| 1,3-Dimethyl-5-ethylbenzene | 0,30                  | 1,3-Dimethyl-5-ethylcyclohexane | 0,31                  |
| Indan                       | 0,04                  | Hydrindan                       | 0,04                  |
| 1,2-Diisopropylbenzene      | 0,15                  | 1,2-Diisopropylcyclohexane      | 0,15                  |
| 1,3-Diisopropylbenzene      | 0,30                  | 1,3-Diisopropylcyclohexane      | 0,31                  |
| Total                       | 4,65                  |                                 |                       |

Interpreted 4.65 or 63%

Not interpreted 2.75 or 37%

From the data of Table 3 it is seen that indan (hydrindan) is present in fractions III and IV, and its homologs in fractions VII and IX.

The residue from the distillation was distilled from a Wurtz flask and the fraction 205-220° removed, from which naphthalene (m. p. 80°) was isolated by the picrate method, this indicating a decalin content in the ligroin. The individual composition of aromatic "A<sub>N</sub>" is shown in Table 4.

From Table 4 it is seen that 18 hexahydro aromatic hydrocarbons were detected by optical analysis. n-Propylcyclohexane was the most abundant C<sub>9</sub> isomer, the ratio of this hexane to isopropylcyclohexane being 3:1. 1-Methyl-4-propylcyclohexane and n-butylcyclohexane predominated among C<sub>10</sub> isomers. Comparing Tables 2 and 4, we see that all three trimethylbenzenes were present in the ligroin, and only two trimethylcyclohexane isomers; 1,3,5-trimethylcyclohexane was not observed.

Yield and properties of the narrow fractions of naphtheno-paraffin hydrocarbons obtained are shown in Table 5.

TABLE 5

| Fraction | Boiling ranges, °C | Content in ligroin, % | $d_4^{20}$ | $n_D^{20}$ | Hydrocarbon content |           |
|----------|--------------------|-----------------------|------------|------------|---------------------|-----------|
|          |                    |                       |            |            | naphthenes          | paraffins |
| I        | 147 —149           | 1,96                  | 0,7395     | 1,4119     | 0,86                | 1,10      |
| II       | 149 —153           | 2,15                  | 0,7384     | 1,4128     | 0,60                | 1,55      |
| III      | 153 —157           | 2,01                  | 0,7434     | 1,4156     | 0,42                | 1,59      |
| IV       | 157 —162,5         | 7,20                  | 0,7470     | 1,4173     | 2,66                | 4,54      |
| V        | 162,5 —166         | 2,64                  | 0,7517     | 1,4194     | 0,90                | 1,74      |
| VI       | 166 —170           | 9,38                  | 0,7495     | 1,4198     | 2,44                | 6,94      |
| VII      | 170 —172           | 1,67                  | 0,7492     | 1,4189     | 0,50                | 1,17      |
| VIII     | 172 —175           | 7,23                  | 0,7424     | 1,4165     | 1,45                | 5,78      |
| IX       | 175 —179           | 3,34                  | 0,7491     | 1,4193     | 0,60                | 2,74      |
| X        | 179 —184           | 5,11                  | 0,7609     | 1,4242     | 2,34                | 2,77      |
| XI       | 184 —190           | 4,32                  | 0,7668     | 1,4271     | 2,20                | 2,12      |
| XII      | 190 —194           | 6,62                  | 0,7667     | 1,4250     | 3,51                | 3,11      |
| XIII     | 194 —197           | 9,83                  | 0,7521     | 1,4218     | 0,88                | 8,95      |
| XIV      | 197 —203           | 2,21                  | 0,7726     | 1,4293     | 1,15                | 1,06      |
| Residue  |                    | 2,21                  |            |            |                     |           |
| Losses   |                    | 0,22                  |            |            |                     |           |
| Total    |                    | 68,10                 |            |            | 20,51               | 45,16     |

TABLE 6

| Hydrocarbon groups  | Amount of hydrocarbons | Content, % |
|---|------------------------|------------|
| Normal C <sub>9</sub> -C <sub>11</sub> hydrocarbons         | 3                      | 16,28      |
| Branched C <sub>10</sub> -C <sub>12</sub> hydrocarbons      | —                      | 28,88      |
| Pentamethylene C <sub>9</sub> -C <sub>11</sub> hydrocarbons | —                      | 20,51      |
| Hexamethylene C <sub>9</sub> -C <sub>12</sub> hydrocarbons  | 17                     | 4,80       |
| Condensed naphthenes  | 2                      | 0,04       |
| C <sub>9</sub> -C <sub>10</sub> benzene derivatives         | 17                     | 9,37       |
| Condensed C <sub>9</sub> -C <sub>10</sub> aromatics         | Possibly               |            |
| Total   | 39                     | 79,88      |

The main point seen from Table 5 is that the ligroin contained 45% of paraffin and 20% of pentamethylene hydrocarbons. Fifty percent of the naphtheno-paraffin portion "NP" is composed of fractions IV, VI, VIII, XIII, which consist mainly of paraffin hydrocarbons; fraction VIII contains 80% — n-decane, and fraction XIII — 90% n-undecane, the amount of the latter being 1.5 times greater than that of n-decane, although total amount of C<sub>10</sub> and C<sub>11</sub> paraffin hydrocarbons is nearly identical (21.7 and 19.7%, respectively). Distribution of the groups in the composition of the ligroin is shown in Table 6.

In all, 39 hydrocarbons were observed, viz.: 17 benzene derivatives, 2 condensed naphthenes (decalin and hydrindan), and 17 hexamethylene hydrocarbons.

#### SUMMARY

1. During investigation of the composition of the ligroin from Romashkin petroleum, the ligroin boiling from 150 to 200°, 18 aromatic and 19 naphthenic hydrocarbons were observed and their content determined.

2. Total paraffin and pentamethylene hydrocarbon content was determined; determination of their individual composition does not appear possible.

#### LITERATURE CITED

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2. C. C. Martin and A. Sankin, *Analyt. Chem.* 25, 206 (1953).
3. B. T. Brucke, S. E. Burd, S. S. Kurtz, and L. Schmerling, *Chemistry of Petroleum Hydrocarbons* [Russian translation], Vol. 1, translated under the editorship of M. M. Kusakov, 1958, pp. 23-24.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

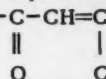
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# KISHNER SYNTHESIS OF DI-, TRI-, AND TETRASUBSTITUTED CYCLOPROPANE HYDROCARBONS

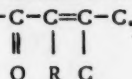
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N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR  
Translated from *Izvestiya Akademii Nauk SSSR, Otdeleniye Khimicheskikh Nauk*,  
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Original article submitted July 22, 1959

In 1910-1911, Kishner [1,2] discovered the method of synthesis of hydrocarbons of the  $C_nH_{2n+2}$  and  $C_nH_{2n}$  series consisting in the catalytic decomposition of alkylidenhydrazines and pyrazolines upon heating in the presence of potassium hydroxide or potassium hydroxide and platinum. Only in 1912, Wolff [3] decomposed alkylidenhydrazines with sodium ethoxide, and his name, without sufficient justification, became associated in the literature with the name of the Kishner reaction.

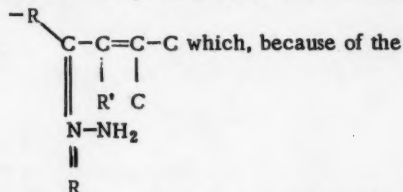
Kishner's reaction found the widest application in organic synthesis, and its mechanism was elucidated in a series of papers [4, 5, 6]. We decomposed pyrazoline bases by Kishner's method in order to prepare the corresponding ditetraalkylsubstituted derivatives of cyclopropane. It is noteworthy that Kishner had already noticed the ease of formation of pyrazoline bases from mesityl oxide and its homologs containing the group



obtained such homologs from acid chlorides and isobutylene as described by Kondakov [5]. This reaction leads to the formation, together with mesityl oxide homologs, mostly of  $\beta$ -chloroketones. The latter, similarly to unsaturated ketones, react with hydrazine to give 3,5,5-pyrazolines [7, 8, 9] which yield, upon decomposition, 1,1,2-trisubstituted cyclopropane derivatives. For the preparation of 1,1,2,3-tetrasubstituted alkyl derivatives of cyclopropane, we used  $\alpha, \beta$ -alkyl substituted unsaturated ketones of the type



The formation of 3,4,5,5-tetrasubstituted pyrazoline derivatives from such ketones and hydrazine hydrate occurs rather slowly, with weak evolution of heat and low yields. This is due to the fact that hydrazine first reacts with an  $\alpha, \beta$ -unsaturated ketone to give a hydrazone of the unsaturated type, viz.,



screening influence of the radical  $R'$  next to the double bond, is slowly converted into 3,4,5,5-tetraalkylpyrazoline, and reacts much more rapidly with a second molecule of the ketone forming a ketazine and polymerization products. In comparison with, for instance, 3,5,5-trialkylpyrazolines, because of the increased steric hindrances during composition, 3,4,5,5-tetraalkylpyrazolines lead to lower yields of 3,4,5,5-tetraalkylcyclopropanes. As shown by Kishner, alkylidenhydrazines are easily split upon heating in the presence of potassium hydroxide, and it is necessary to add the alkali slowly and dropwise in order to avoid an explosive decomposition. As a rule, pyrazoline derivatives are rather stable compounds, and they decompose with difficulty upon continuous heating. Their decomposition is attained by different methods: by prolonged heating in sealed ampuls [3] or in an autoclave [10], by heating in a flask with a high-boiling solvent [11, 12], or in a catalytic furnace over potassium hydroxide [13], and, finally, by heating in a flask in the absence of catalysts [9]. In the present work, we decomposed pyrazoline derivatives by a method analogous to that used for the decomposition of alkylidenhydrazines.

## EXPERIMENTAL

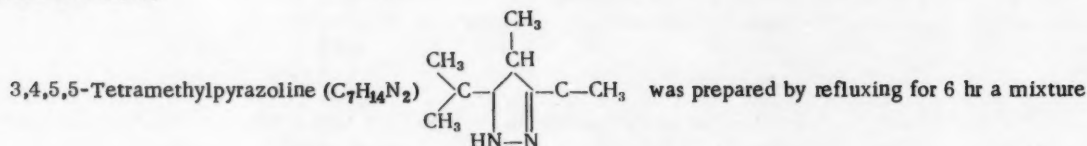
The bases were decomposed in a long-necked 100 ml copper flask fitted with a tube for the insertion of a thermometer. The flask was connected to a two-necked adapter. In one of the necks of the adapter was fitted a dropping funnel with a long stem ending 2.5 cm above the layer of potassium hydroxide in the flask. The other neck was connected to a fractionating column (fitted with a thermometer), a condenser pointing downwards and cooled with ice, and a trap placed in a Dewar bottle filled with dry ice. The flask was charged with 30-50 g of dry potassium hydroxide (preliminarily dried by heating in a copper crucible at 300-350°), and heated to 270-310°. This temperature was maintained throughout the experiment. The pyrazoline base was slowly added from the dropping funnel. Its decomposition was accompanied by a continuous evolution of nitrogen. The hydrocarbon produced during the reaction, together with a small amount of the starting material, was dried over  $K_2CO_3$ , and distilled in a Favorskii flask to remove the base. The distilled hydrocarbon was washed with an equal volume of 50% acetic acid to remove the last traces of the base. After washing with alkali and water, the product was dried again over anhydrous potassium carbonate and distilled, first as such, and then, 3 to 5 times with the addition of metallic sodium, using fractionating columns with efficiencies of the order of 18-38 theoretical plates. Raman spectra were recorded for all the hydrocarbons obtained in these experiments.

First, in order to adjust the experimental conditions, 3,5,5-trimethylpyrazoline was decomposed to 1,1,2-trimethylcyclopropane, b. p. 52.5° (745 mm);  $d_4^{20}$  0.6944;  $n_D^{20}$  1.3868. Reported b. p. 52.8°;  $d_4^{20}$  0.6927;  $n_D^{20}$  1.3872 [14].

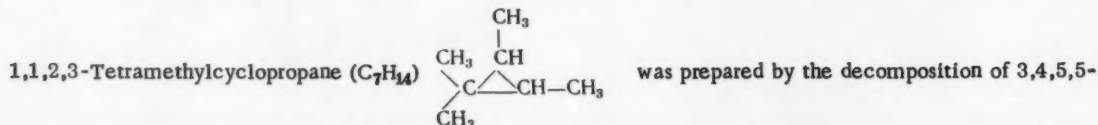
Then, the following pyrazoline bases were prepared and decomposed to the corresponding cyclopropane hydrocarbons:

1. 4-Chloro-3,4-dimethylpentane-2-one ( $C_7H_{13}OCl$ )  $\begin{array}{c} Cl \\ | \\ CH_3-C-CH-C-CH_3 \\ | \quad | \quad || \\ CH_3 \quad CH_3 \quad O \end{array}$  was obtained from trimethyl-

ethylene and acetyl chloride by Kondakov's method, b. p. 55° (16 mm);  $d_4^{20}$  0.9745;  $n_D^{20}$  1.4414; found MR 38.91; calculated MR 39.40.



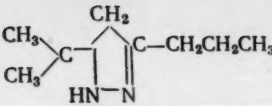
of 92 g of the chloroketone, 50 g of hydrazine hydrate, and 50 ml of ethyl alcohol; b. p. 68-70° (15 mm);  $d_4^{20}$  0.9036;  $n_D^{20}$  1.4600; found MR 38.60; calculated MR 38.07; yield 50%.



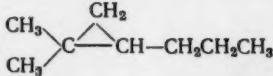
tetramethylpyrazoline, b. p. 77-78°;  $d_4^{20}$  0.7193;  $n_D^{20}$  1.4020; found MR 33.114; calculated MR 33.118 (acc. to Vogel [15]). Found: C 85.7; H 14.30%. Calculated: C 85.63; H 14.37%.

2. 2-Chloro-2-methylheptane-4-one ( $C_8H_{15}OCl$ )  $\begin{array}{c} Cl \quad O \\ | \quad || \\ CH_3-C-CH_2-C-CH_2CH_2CH_3 \\ | \\ CH_3 \end{array}$  was prepared from butyryl

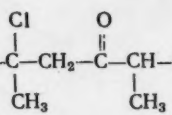
chloride and isobutylene in the presence of 10%  $ZnCl_2$  by stirring the reaction mixture at 0° for 2 days. Yield, 45.8%; b. p. 59-63° (15 mm);  $d_4^{20}$  0.8660; for  $n_D^{20}$  1.4470.

3-Propyl-5,5-dimethylpyrazoline ( $C_8H_{16}N_2$ )  was prepared from 101 g of 2-chloro-

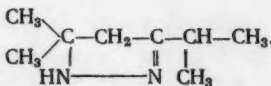
2-methylheptane-4-one and 57 g of hydrazine hydrate in alcohol by refluxing the reaction mixture for 6 hr on a water bath. The base boiled at 67-68° (7 mm);  $d_4^{20}$  0.8856;  $n_D^{20}$  1.4583; found MR 43.23; calculated MR 43.22; yield 91%.

1,1-Dimethyl-2-propylcyclopropane ( $C_8H_{16}$ )  was prepared by the catalytic decom-

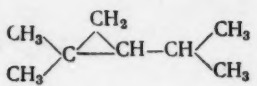
position of 79 g of 3-propyl-5,5-dimethylpyrazoline at 260-270°. After usual treatment and five-fold distillation over sodium metal, the product boiled at 105.5° (745 mm);  $d_4^{20}$  0.7292;  $n_D^{20}$  1.4060; found MR 37.79; calculated MR 37.704; yield 42.8%. Found: C 85.94; H 14.20%. Calculated: C 85.63; H 14.37%.

3. 5-Chloro-2,5-dimethylcyclohexane-3-one ( $C_8H_{15}OCl$ )  was synthesized from

isobutyryl chloride and isobutylene in the presence of 10%  $ZnCl_2$ . Yield, 28%; b. p. 62-70° (12 mm);  $d_4^{20}$  0.9049;  $n_D^{20}$  1.4390.

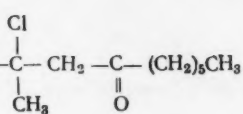
3-Isopropyl-5,5-dimethylpyrazoline ( $C_8H_{16}N_2$ )  was prepared from 50 g of 5-chloro-

2,5-dimethylcyclohexane-3-one, and an alcoholic solution of 23.1 g of hydrazine hydrate. Yield, 38 g (88%), b. p. 85-86° (12 mm);  $d_4^{20}$  0.8801;  $n_D^{20}$  1.4543; found MR 43.08; calculated MR 43.85 (acc. to Vogel).

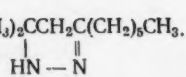
1,1-Dimethyl-2-isopropylcyclopropane ( $C_8H_{16}$ )  was obtained by the catalytic de-

composition of 38 g of 3-isopropyl-5,5-dimethylpyrazoline at 280-300°. After usual treatment and repeated distillation over metallic sodium, 15 g (49.3%) of 1,1-dimethyl-2-isopropylcyclopropane was obtained, b. p. 94-95° (762 mm);  $d_4^{20}$  0.7137;  $n_D^{20}$  1.3970; found MR 37.56; calculated MR 37.76. Found: C 85.84; H 14.16%. Calculated: C 85.63; H 14.37%.

Decomposition in the absence of the catalyst led to an identical product (from the point of view of properties and Raman spectra).

4. 2-Chloro-2-methyldecane-4-one ( $C_{11}H_{21}OCl$ )  was prepared from the acid

chloride of enanthic acid and isobutylene in the presence of  $ZnCl_2$ . Yield, 47.8%; b. p. 99-100° (8 mm);  $d_4^{20}$  0.8844;  $n_D^{20}$  1.4430.

3-Hexyl-5,5-dimethylpyrazoline ( $C_{11}H_{22}N_2$ )  was prepared by adding 85 g of 2-chloro-

2-methyldecane-4-one to 56 g of hydrazine hydrate in 56 ml of ethyl alcohol, and refluxing the mixture for 6 hr with stirring. After distillation of the reaction product, 61 g (82%) of the pyrazoline derivative was obtained, b. p. 106-107° (7 mm);  $d_4^{20}$  0.8736;  $n_D^{20}$  1.4598; found MR 57.14; calculated MR 57.07.

1,1-Dimethyl-2-hexylcyclopropane ( $C_{11}H_{22}$ )  $(CH_3)_2C(CH_2)_5CH_3$  was prepared by the decomposition

of 80.5 g of 3-hexyl-5,5-dimethylpyrazoline at 250-270° in the presence of 40 g of potassium hydroxide. After usual treatment and four-fold distillation over sodium with a fractionating column of 38 theoretical plates, 39.6 g of 1,1-dimethyl-2-hexylcyclopropane was obtained, b. p. 176.5° (736 mm);  $d_4^{20}$  0.7612;  $n_D^{20}$  1.4240; found MR 51.65; calculated MR 51.61. Found: C 85.74; H 14.32%. Calculated: C 85.63; H 14.37%.

5. 2-Chloro-2-methyl-5-ethylnonane-4-one ( $C_{12}H_{23}OCl$ )  $CH_3-C(CH_3)(Cl)-CH_2-C(=O)-CH(CH_2)_2CH_3$  was prepared from

the acid chloride of  $\alpha$ -ethylcapronic acid and isobutylene in the presence of 10%  $ZnCl_2$  (method [5]). Yield 62%; b. p. 120-125° (5 mm);  $d_4^{20}$  0.9021;  $n_D^{20}$  1.4465.

3-(1'-Ethylpentyl)-5,5-dimethylpyrazoline ( $C_{12}H_{24}N_2$ )  $CH_3-C(CH_3)(HN)-CH_2-C(=N)-CH(CH_3)-CH_2-CH_2-CH_2-CH_3$  was pre-

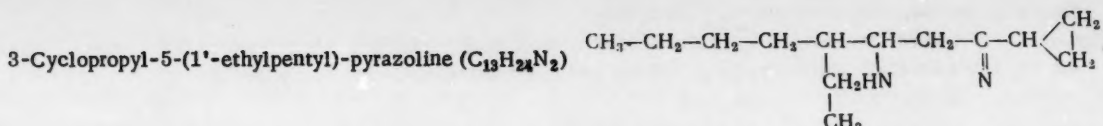
pared as follows: 34.4 g of hydrazine hydrate in 50 ml of ethanol was treated with 100 g of 2-chloro-2-methyl-5-ethylnonane-4-one in 70 ml of alcohol. The mixture was refluxed for 6 hr at 80°, with stirring. After alcohol and hydrazine hydrate were driven off by distillation, 75.8 g (84.4%) of the pyrazoline base was obtained, b. p. 143-144° (20 mm);  $d_4^{20}$  0.8748;  $n_D^{20}$  1.4580; found MR 61.12; calculated MR 61.68.

1,1-Dimethyl-2-(1'-ethylpentyl)cyclopropane ( $C_{12}H_{24}$ )  $(CH_3)_2C(CH_2)_5CH_3$  was pre-

pared by the thermal decomposition of 84 g of 3-(1'-ethylpentyl)-5,5-dimethylpyrazoline at 290° in the absence of a catalyst. The hydrocarbon thus produced was distilled at 190-200°, washed with 50% acetic acid to remove any undecomposed base, neutralized with a 25% solution of sodium hydroxide, washed with water, dried over calcium chloride, and distilled twice over metallic sodium. Yield of 1,1-dimethyl-2-(1'-ethylpentyl)cyclopropane, 52 g (65%); b. p. 186.5-187.5°;  $d_4^{20}$  0.7738;  $n_D^{20}$  1.4309; found MR 56.15; calculated MR 56.35. Found: C 85.59; H 14.45%. Calculated: C 85.63; H 14.37%.

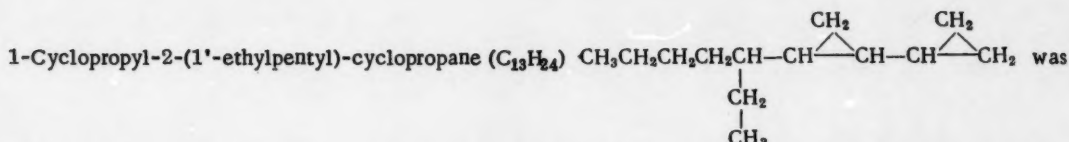
6. 3-Ethyl-1-heptenylcyclopropyl ketone ( $C_{13}H_{22}O$ )  $CH_3-CH_2-CH_2-CH_2-CH(CH_2CH_3)-CH=CH-C(=O)-CH(CH_2)_2$  A

mixture of 50 g of methyl cyclopropyl ketone, 1 g of KOH, and 10 ml of ethanol was treated dropwise during 2 hr, while stirring and cooling the flask with water, with 64 g of 2-ethylhexaldehyde [ $d_4^{20}$  0.8388,  $n_D^{20}$  1.4320; found MR 38.92; calculated MR 39.20 (acc. to Vogel)]. 2,4-dinitrophenylhydrazine m.p. 122°. Stirring was continued without cooling for a further period of 10 hr. After 2 days, the contents of the flask were poured on 400 ml of water, and the mixture thus obtained extracted thrice with ether. The combined ethereal extracts were dried over  $CaCl_2$ , the solvent driven off, and the residue distilled in vacuum. Yield, 40.8 g (41.2%) of the ketone, b. p. 141° (17 mm);  $d_4^{20}$  0.8870;  $n_D^{20}$  1.4715; found MR 61.28; calculated MR 60.49. Found: C 80.30, 80.47; H 11.60, 11.60%.  $C_{13}H_{22}O$ . Calculated: C 80.35; H 11.41%.



was prepared by adding 34 g of 3-ethyl-1-heptenylcyclopropyl ketone to a solution of 17 g of hydrazine hydrate in 20 ml of ethanol. The temperature of the reaction mixture rose during the addition from 21 to 48°. Then it was heated with stirring on a water bath at 80° for 5.5 hr. Finally, the lower layer of the mixture was separated, and the upper layer was distilled in vacuum. Yield of 3-cyclopropyl-5-(1'-ethylpentyl)-pyrazoline, 26 g (71.4%); b. p. 131° (5 mm);  $d_4^{20}$  0.9269;  $n_D^{20}$  1.4880; found MR 64.75; calculated MR 63.06.

As the newly synthesized pyrazoline bases decompose even upon standing at room temperature, their elemental analysis was dispensed with.



prepared as follows: 26 g of 3-cyclopropyl-5-(1'-ethylpentyl)-pyrazoline was added to 10 g of KOH heated to 260-270° at such a rate as to keep the temperature of the vapors issuing from the rectifying column below 160-180°. The distillate thus obtained (14 ml) was washed thrice with 50% acetic acid (10 ml portions), neutralized with sodium carbonate, and dried over KOH. The acid extract yielded 3 g of the recovered pyrazoline base. The 1-cyclopropyl-2-(1'-ethylpentyl)-cyclopropane obtained in this experiment was distilled once without adding sodium metal, and twice in vacuum over sodium. As the Raman spectrum of this product revealed the presence of a small amount of contaminating alkenes, the latter were removed by oxidation with 1% potassium permanganate. After steam distillation, extraction with ether, drying over  $\text{CaCl}_2$ , and distillation of the solvent, the resulting product was twice distilled in vacuum over sodium metal. Yield of 1-cyclopropyl-2-(1'-ethylpentyl)-cyclopropane, 7 g (35%); b. p. 111° (24 mm);  $d_4^{20}$  0.8178;  $n_D^{20}$  1.4485; found MR 59.08; calculated MR 59.53. Found: C 86.61, 86.86; H 13.11, 13.10%. Calculated: C 86.58; H 13.41%.

#### SUMMARY

1. 1,1,2,3-Tetramethylcyclopropane; 1,1-dimethyl-2-propylcyclopropane; 1,1-dimethyl-2-isopropylcyclopropane; 1,1-dimethyl-2-hexylcyclopropane; 1,1-dimethyl-2-(1'-ethylpentyl)cyclopropane; and 1-cyclopropyl-2-(1'-ethylpentyl)cyclopropane were synthesized for the first time.

2. As the structure of the  $\alpha, \beta$ -unsaturated ketone becomes more complicated, and  $\alpha$ -substituents are introduced into the molecule, the screening effect over the double bond during the reaction with hydrazine becomes more important, and considerably hinders the formation of the pyrazoline base.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

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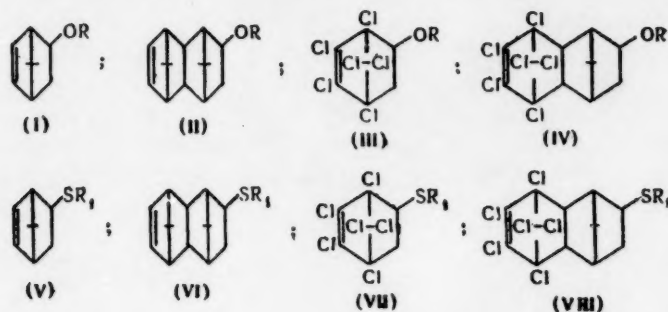
# VINYL COMPOUNDS IN DIENE SYNTHESIS

## COMMUNICATION 4. COMPARATIVE CHARACTERIZATION OF THE DIENOPHILE ACTIVITY OF VINYL AND THIOVINYL ETHERS, AND OPTICAL INVESTIGATION OF THE ADDUCTS OBTAINED

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We have shown earlier the possibility of carrying out a diene synthesis with cyclopentadiene and hexachlorocyclopentadiene using vinyl and thiovinyl ethers containing alkyl and aromatic radicals in the role of dienophile component [1-3]. This allowed the synthesis of a series of derivatives of bicyclo-[2,2,1]hept-5-ene and 1,4,5,8-diendomethylene-1,2,3,4,4a,5,8,8a-octahydronaphthalene of the general structure:





where  $R = C_2H_5$  (a);  $C_4H_9$  (b);  $C_6H_{11}$  (cycl.) (c);  $C_{10}H_{17}$  ( $\beta$ ) (d);  $C_6H_5$  (e);  $C_6H_4C_4H_9$  (p-tert.) (f);  $C_{10}H_7$  (g), and  $R_1 = C_2H_5$  (a);  $C_4H_9$  (b);  $C_6H_5$  (c).

Thiovinyl ethers and vinyl esters were considered by Alder [4] as belonging to a group of less active dienophiles having a polar group next to the double bond. Probably, vinyl ethers also belong to this group. However, it was interesting to elucidate their dienophile activity in relation to the structure of the radical, and the nature of the heteroatom. Therefore, to complete our earlier study of vinyl and thiovinyl ethers containing alkyl and aryl groups, in the present communication we discuss the diene synthesis with cyclopentadiene and hexachlorocyclopentadiene using as dienophiles the following ethers containing hydroaromatic radicals: Vinyl cyclohexyl ether, vinyl  $\beta$ -decalyl ether, as well as vinyl ethyl ether and vinyl butyl sulfide. No adduct was isolated when cyclopentadiene was condensed with vinyl ethyl ether, but in the other cases, new derivatives were obtained, viz., of bicycloheptene (Ic, Id, and Vb), octahydronaphthalene (IIc, and Vb), hexachlorobicycloheptene (IIIb, IIIc, and IIId), and dihydraldrene (IVc and IVd). In order to characterize some of the adducts synthesized from cyclopentadiene, we prepared their hydrogenated derivatives, viz., the corresponding norcamphanes, and their condensation products with phenylazide, viz., the corresponding dihydrotriazole derivatives; the latter were also prepared from thioethyl- and thio-phenyldiendomethyleneoctahydronaphthalenes.

A comparison between the dienophile activity of vinyl and thiovinyl ethers revealed a noticeable difference in relation to the character of the radical and the heteroatom. It appeared that the most active compounds in diene synthesis with cyclopentadiene and hexachlorocyclopentadiene are vinyl ethers which contain aromatic radicals,

ethers with alkyl and hydroaromatic radicals being less reactive. In the latter case the yield of the adduct is lowered because of the thermal decomposition of the starting ether under the conditions of the reaction. The introduction of a heteroatom in a dienophile, and the nature of the heteroatom also influence the reactivity of vinyl ethers in diene synthesis. It is known that ethylene participates in diene synthesis only under conditions of high temperature and pressure [5, 6]. Vinyl alkyl ethers [7, 1] condense with dienes comparatively easier. The diene synthesis with thiovinyl ethers occurs smoothly and with a good yield [2]. These considerations are confirmed by the data of Table 1 which gives the percent conversion of vinyl and thiovinyl ethers into the adducts (I) and (II) upon condensation with cyclopentadiene. In all the reactions we used a two-fold excess of vinyl ether, and the yields are calculated on the basis of the ether which entered the reaction.

TABLE 1. Conversion of Vinyl and Thiovinyl Ethers into Adducts

| Vinyl ethers   | Reaction temperature, °C | Duration of the reaction in hr | Yield of the adduct in %  |   | Conversion of the starting ether into adducts in % |
|--|--------------------------|--------------------------------|---|---|--|
|  |                          |                                |  |  |  |
| $\text{CH}_2=\text{CH}-\text{O}-\text{C}_6\text{H}_5$                              | 180—195                  | 16                             | Adduct not formed   |   | —  |
| $\text{CH}_2=\text{CH}-\text{O}-\text{C}_4\text{H}_9$                              | 180—190                  | 15                             | 23  | 10  | 33   |
| $\text{CH}_2=\text{CH}-\text{O}-\text{C}_6\text{H}_{11}$                           | 180—185                  | 15                             | 27  | 4   | 31   |
| $\text{CH}_2=\text{CH}-\text{O}-\text{C}_{10}\text{H}_{17}$ ( $\beta$ )            | 180—185                  | 15*                            | 15  | —   | 15   |
| $\text{CH}_2=\text{CH}-\text{O}-\text{C}_6\text{H}_5$                              | 165—170                  | 13                             | 76  | 18  | 94   |
| $\text{CH}_2=\text{CH}-\text{O}-\text{C}_6\text{H}_4\text{C}_3\text{H}_9$ (p-tert) | 165—170                  | 13                             | 62  | 33  | 95   |
| $\text{CH}_2=\text{CH}-\text{O}-\text{C}_{10}\text{H}_7$ ( $\beta$ )               | 165—170                  | 13                             | 72  | 15  | 87   |
| $\text{CH}_2=\text{CH}-\text{S}-\text{C}_2\text{H}_5$                              | 160—165                  | 12                             | 60  | 14  | 74   |
| $\text{CH}_2=\text{CH}-\text{S}-\text{C}_4\text{H}_9$                              | 160—165                  | 12                             | 59  | 13  | 72   |
| $\text{CH}_2=\text{CH}-\text{S}-\text{C}_6\text{H}_5^*$                            | 160—165                  | 12                             | 67  | 13  | 80   |

\*Because of the lower thermal stability of vinyl phenyl sulfide in comparison with its oxygen analog, it is not possible to recover all the excess of this substance from the reaction products; therefore, the given percent conversion of this ether is lower than the actual amount.

For a more complete characterization of the adducts of vinyl and thiovinyl ethers with cyclopentadiene and hexachlorocyclopentadiene, we carried out their spectroscopic investigation. The infrared and Raman spectra of bicyclo-(2,2,1)heptene and 1,4,5,8-diendomethylene-1,2,3,4,4a,5,8,8a-octahydronaphthalene structures were studied. The frequencies of the absorption bands of infrared spectra and their interpretation for all the compounds investigated are given in Table 2. Some of these spectra (marked in Table 2 with an asterisk) are not complete because of the superposition of the absorption bands of the solvent (chloroform) on the bands of the substance investigated. For the majority of compounds under study, only a few of the absorption bands could be related to definite functional groups and bonds with a sufficient degree of certitude.

The spectra of the majority of compounds show, in the  $1620\text{--}1560\text{ cm}^{-1}$  region, the absorption band due to the double bond; the frequency of this band is considerably lower than that of cycloolefins, and this fact, according to the literature [8, 9], is characteristic for a bicycloheptene ring. By taking into consideration the fact that in Raman spectra the valency vibration is reflected better, we recorded these spectra for a series of compounds. The frequencies of the lines of the Raman spectra thus obtained are given in Table 3.

The Raman spectra display intense lines in the frequency region ( $1560\text{--}1620\text{ cm}^{-1}$ ) of the double bond, which are split in some compounds into several components. The magnitude of splitting is equal to  $40\text{--}50\text{ cm}^{-1}$ . This effect cannot be explained by the occurrence of endo-exo isomerism, as Kohlrausch and Seka [10] have shown that substituents in position 2 and 3 cause only a negligible displacement of the double bond frequency of the bicycloheptene ring. Moreover, our measurements of the double bond frequencies of samples of 2-phenoxybicyclo-(2,2,1)hept-5-ene enriched with exo- and endo- isomers show that these frequencies differ only by a few  $\text{cm}^{-1}$ . An explanation of the splitting of lines only on the basis of Fermi resonance is not very convincing: first, because the frequencies are split not only to two, but to three components; second, because the displacement of frequencies in comparison with samples which do not display splitting of lines is observed only for one of the components. Apparently, the phenomenon of

splitting of double bond frequencies is due essentially to a possibility of the existence of sterically isomeric forms of the bicycloheptene ring itself.

TABLE 2. Infrared Spectra of Adducts of Vinyl and Thiovinyl Ethers

| Adduct  | (IIIg*)                      | (VIIc*)                      | (Id)   | (IIe*)   | (IIb)   | (IIg*)   | (Ig*)                                | (VIc*)                               | (VIa)                | (Ib)       |
|---|------------------------------|------------------------------|--|--|---|--|--------------------------------------|--------------------------------------|----------------------|------------|
| Frequencies of absorption bands (cm <sup>-1</sup> ) |                              | 706                          | 634<br>662<br>683<br>730                             | 695<br>718   | 630<br>679<br>706<br>729                      | 632<br>661<br>680                                    |                                      | 694                                  | 744                  | 724        |
|   |                              |                              | 761<br>787<br>813<br>832<br>853<br>898               |  | 739<br>755<br>794<br>812<br>844<br>896<br>912 |  | 769                                  |                                      | 786                  | 752<br>782 |
|   | 834<br>864<br>894<br>912     | 851<br>867<br>912            |  | 856<br>882<br>900  |   | 836  | 832                                  | 856                                  | 840                  | 844        |
|   |                              |                              |  |  |   | 896  | 910                                  | 900                                  | 904                  | 912        |
|   | 924<br>964<br>1002           | 971<br>985<br>1010           | 942<br>970<br>984                                    | 962<br>984<br>998  | 972<br>984                                    | 919<br>960<br>994                                    | 956                                  | 962                                  |                      |            |
|   |                              |                              |  |  |   |  | 994                                  | 1008                                 | 1012                 |            |
|   | 1105<br>1125<br>1179         | 1028<br>1065<br>1096<br>1154 | 1028<br>1076<br>1088<br>1117<br>1120<br>1152<br>1260 | 1024<br>1076<br>1088<br>1120<br>1159<br>1249<br>1318<br>1364 |   | 1043<br>1111<br>1120<br>1178<br>1215<br>1250<br>1360 | 1040<br>1068<br>1120<br>1176<br>1258 | 1024<br>1064<br>1088<br>1128<br>1140 | 1042                 |            |
|   | 1214<br>1256<br>1359<br>1396 | 1278                         | 1352   | 1364   |   | 1362<br>1394   | 1365<br>1396<br>1445                 | 1322                                 | 1250<br>1318<br>1352 | 1272       |
|   |                              | 1448                         | 1454   |  |   |  |                                      |                                      | 1448                 |            |
|   | 1473<br>1526                 | 1487                         |  |  | 1470  | 1478   | 1475                                 | 1480                                 |                      |            |
|   |                              | 1610                         |  | 1494<br>1568<br>1612   |   | 1512   | 1518<br>1602                         | 1594                                 | 1544                 |            |

In the spectra of the majority of substances possessing either a bicycloheptene or a diendomethyleneoctahydronaphthalene structure, we observed intense absorption lines in the region of 710-740 cm<sup>-1</sup> (14-13.5  $\mu$ ); this is in good agreement with published data [11-13]. The infrared spectra, as well as Raman spectra, displayed a frequency in the region of 895-910 cm<sup>-1</sup>. According to Aleksanyan and Sterin [8], this frequency must be ascribed to the pulsational vibration of the five-membered ring. We noticed that the infrared spectra of the substances under investigation have an intense absorption band in the region of 990-1010 cm<sup>-1</sup>. Apparently, this band must be ascribed to a deformation vibration of the CH group in the neighborhood of the double bond. A comparison with the spectra of cycloolefins shows that this region of the frequency of the given vibration is rather specific for the bicycloheptene structure.


#### EXPERIMENTAL

##### Condensation of Vinyl Ethers Containing Hydroaromatic Radicals with Cyclopentadiene

Vinyl  $\beta$ -decalyl ether. Cyclopentadiene (6.6 g, 0.1 mole) and vinyl ether (36.2 g, 0.2 mole) were heated together in an autoclave at 175-180° for 15 hr. The reaction mixture was steam-distilled, and two fractions were obtained. Fraction I boiling at 104-118° (5 mm) consisted of a mixture of the starting ether (21.1 g) and  $\beta$ -decalol. Fraction II (15 g) boiling at 130-200° (4 mm) gave, after heating with 2% H<sub>2</sub>SO<sub>4</sub> for removing acetal, 6.5 g of 2- $\beta$ -decaloxybicyclo-(2,2,1)-hept-5-ene (Id) which appeared as a colorless liquid with a camphane smell, b. p.

162-164° (4 mm);  $n_D^{20}$  1.5125;  $d_4^{20}$  1.043; found MR 72.76.  $C_{17}H_{26}O$ . calculated MR 73.08. Found: C 83.08, 83.00; H 10.51, 10.40%. Calculated: C 82.87; H 10.64%.

TABLE 2 (continued)

| (Ic)                         | (Va)   | (II <sub>f</sub> <sup>*</sup> )                                      | (If <sup>*</sup> )   | (Id)   |  | Functional group or bond   |
|------------------------------|--|--|--|--|--|--|
|                              |  |  |  | exo-   | endo-  |  |
| 724                          | 712<br>732   | 692  |  | 706<br>724   | 695  |  |
| 752<br>782<br>844<br>906     | 764<br>808<br>882<br>906   | 841<br>891<br>903  | 828  | 752<br>800<br>824<br>852<br>880<br>908                                       | 857<br>885<br>906  | Pulsational vibration of the<br>five-membered ring                                 |
| 952<br>1000                  | 942<br>992   | 992  | 992  | 949<br>968<br>984<br>996   | 964<br>994   |  |
| 1090<br>1180<br>1272<br>1368 | 1048<br>1096<br>1132<br>1184<br>1220<br>1264<br>1322<br>1376<br>1452 | 1008<br>1030<br>1082<br>1114<br>1186<br>1300<br>1318<br>1368<br>1398 | 1042<br>1052<br>1068<br>1116<br>1152<br>1184<br>1292<br>1408 | 1044<br>1074<br>1096<br>1118<br>1170<br>1244<br>1300<br>1344<br>1364<br>1465 | 1041<br>1075<br>1115<br>1154<br>1176<br>1230<br>1288<br>1341<br>1362 |  |
|                              |  | 1475   | 1475   |  |  | CH <sub>2</sub>  |
|                              |  | 1580   | 1581   | 1504<br>1603   | 1501<br>1602   | C=C  |

Yield of the adduct, 15% of the theoretical, based on the ether which entered the reaction (22.1 g). For its spectrum, see Table 2.

Vinyl cyclohexyl ether. A mixture of cyclopentadiene (6.6 g, 0.1 mole) and vinyl ether (25.4 g, 0.2 mole) was heated in an autoclave under analogous conditions. After vacuum distillation of the reaction mixture, and the removal of the acetal by hydrolysis, 10.5 g of the starting ether and 6.1 g of 2-cyclohexoxybicyclo-(2,2,1)hept-5-ene (Ic) was isolated. (Ic) had b. p. 95-98° (2 mm);  $n_D^{20}$  1.5060;  $d_4^{20}$  1.0052; found MR 57.15.  $C_{13}H_{20}O$ . Calculated MR 57.91. Found: C 81.30, 81.22; H 10.47, 10.43%.  $C_{13}H_{20}O$ . Calculated: C 81.10; H 10.56%.

Yield of the adduct, 27% of the theoretical. Spectra data in Tables 2 and 3.

A fraction boiling at 148-150° (2.5 mm) (1.3 g, 4.3% of the theoretical) was also obtained. It consisted of 1,4,5,8-diendomethylene-2-cyclohexoxy-1,2,3,4,4a,5,8,8a-octahydronaphthalene (IIc),  $n_D^{20}$  1.5190;  $d_4^{20}$  1.0492; found MR 74.76.  $C_{19}H_{26}O$ . Calculated MR 75.50. Its crystalline addition product with phenylazide (yield, 68% of the theoretical) melted at 185-187.5° (dec.). Found: N 11.51, 11.67%.  $C_{24}H_{31}N_2O$ . Calculated: N 11.13%.

Vinyl butyl sulfide. A mixture of dicyclopentadiene (6.6 g, 0.05 mole) and vinyl sulfide (23.2 g, 0.2 mole) was heated in an autoclave for 12 hr at 160-165°. Vacuum distillation of the reaction product gave 12.0 g of the starting thioether, 10.3 g (58.6% of the theoretical, calculated on the basis of 11.2 g of thioether which has reacted)

of 2-thiobutylbicyclo-(2,2,1)hept-5-ene (Vb), b. p. 94-94.8° (4 mm);  $n_D^{20}$  1.5076;  $d_4^{20}$  0.9693; found MR 56.04,  $C_{11}H_{18}S$ . Calculated MR 56.12. Found: C 72.56, 72.72; H 9.83, 9.94; S 17.29, 17.27%. Calculated: C 72.46; H 9.95; S 17.59%, and 3.0 g of 1,4,5,8-diendomethylene-2-thiobutyl-1,2,3,4,4a,5,8a-octahydronaphthalene (VIb), (12.5% of the theoretical calculated on the basis of 11.2 g of thioether which has reacted), b. p. 160-160.5° (4.5 mm);  $n_D^{20}$  1.5345;  $d_4^{20}$  1.0392; found MR 74.46,  $C_{16}H_{24}S$ . Calculated MR 74.82. Found: C 77.50, 77.55; H 9.92, 9.83; S 13.15, 13.32%. Calculated: C 77.36; H 9.73; S 12.90%.

A mixture of dicyclopentadiene (3.3 g, 0.025 mole) and vinyl ethyl sulfide (8.8 g, 0.1 mole) was heated in an autoclave at 160-165° for 12 hr.\* The yield of 2-thioethylbicyclo-(2,2,1)hept-5-ene (Va) was 4.1 g (60% of the theoretical, calculated on the basis of the 3.8 g of sulfide which entered the reaction). (Va) had b. p. 60-60.5° (3 mm), and  $n_D^{20}$  1.5158. It was accompanied by 1.3 g (14% of the theoretical, calculated w.r. to the 3.8 g of sulfide which had reacted) of 1,4,5,8-diendomethylene-2-thioethyl-1,2,3,4,4a,5,8a-octahydronaphthalene (VIa), b. p. 135.5-137° (5 mm);  $n_D^{20}$  1.5462.

Under analogous conditions, 3.3 g (0.025 mole) of dicyclopentadiene and 13.6 g (0.1 mole) of vinyl phenyl sulfide gave 6.5 g (66.3% of the theoretical, based on 6.5 g of the sulfide which had reacted) of 2-thiophenylbicyclo-(2,2,1)hept-5-ene (Vc), b. p. 143-144° (6 mm);  $n_D^{20}$  1.5925, and 1.6 g (12.5% of the theoretical w.r. to the 6.5 g of the sulfide which had reacted) of 1,4,5,8-diendomethylene-2-thiophenyl-1,2,3,4,4a,5,8a-octahydronaphthalene (VIc), b. p. 200-201° (4 mm).

#### Condensation of Vinyl Ethers with Hexachlorocyclopentadiene

**Vinyl butyl ether.** A mixture of the ether (3 g, 0.03 mole), and of the diene (8.1 g, 0.03 mole) was heated in a flask fitted with a reflux condenser for 3 hr at 85-95° in the presence of hydroquinone. After removal of unreacted diene 4.2 g, 3.5 g (66% of the theoretical based on the diene which has reacted) of 2-butoxy-1,4,5,6,7,7-hexachlorobicyclo-(2,2,1)hept-5-ene (IIIb) was obtained as a pale yellow liquid with a characteristic unpleasant smell, b. p. 140-141° (2 mm);  $n_D^{20}$  1.5250,  $d_4^{20}$  1.4552; found MR 78.68,  $C_{11}H_{12}Cl_6O$ . Calculated MR 79.00. Found: C 35.08, 35.17; H 3.19, 3.10; Cl 56.94, 56.57%. Calculated: C 35.42; H 3.24; Cl 57.05%.

**Vinyl cyclohexyl ether.** The ester (5.2 g, 0.04 mole) and the diene (5.4 g, 0.02 mole) gave, under analogous conditions, 14.5 g (70% of the theoretical w.r. to the 4.4 g of the diene which entered the reaction) of 2-cyclohexoxy-1,4,5,6,7,7-hexachlorobicyclo-(2,2,1)hept-5-ene (IIIc), b. p. 104-105° ( $8 \cdot 10^{-5}$  mm);  $n_D^{20}$  1.5495. Found: C 39.35, 39.57; H 3.63, 3.49; Cl 52.73, 52.86%.  $C_{13}H_{14}Cl_6O$ . Calculated: C 39.12; H 3.54; Cl 53.30%.

**Vinyl  $\beta$ -decalyl ether.** Under the same conditions, 10.8 g (0.06 mole) of the ether and 8.1 g (0.03 mole) of the diene gave 3.6 g (42% of the theoretical, calculated on the basis of the 5.1 g of the diene which had reacted) of 2- $\beta$ -decaloxy-1,4,5,6,7,7-hexachlorobicyclo-(2,2,1)hept-5-ene (IIId), as a thermally poorly stable, very viscous product with an unpleasant smell, b. p. 138-140° ( $5 \cdot 10^{-3}$  mm). Found: C 44.78, 44.56; H 4.86, 4.75; Cl 46.57; 46.72%.  $C_{17}H_{20}Cl_6O$ . Calculated: C 44.95; H 4.44; Cl 46.85%.

#### Reaction of the Bicycloheptenes with Hexachlorocyclopentadiene

a) The diene (2.7 g, 0.01 mole) and 1.94 g (0.01 mole) of 2-cyclohexoxybicycloheptene (Ic) were heated together for 9 hr at 125-130° in a flask fitted with a reflux condenser. After removal of the portion of starting materials which did not react (containing 0.7 g of the diene), 2.2 g (65% of the theoretical) of 1,4,5,8-diendomethylene-2-cyclohexoxy-5,6,7,8,9,9-hexachloro-1,2,3,4,4a,5,8a-octahydronaphthalene (IVc) was obtained as a very viscous pale yellow product, b. p. 208-210° (1 mm). Found: C 46.63, 46.56; H 4.03, 4.14; Cl 45.99, 46.30%.  $C_{18}H_{20}Cl_6O$ . Calculated: C 46.48; H 4.33; Cl 45.74.

b) Under analogous conditions, 2.7 g (0.01 mole) of the diene and 1.8 g (0.01 mole) of 2- $\beta$ -decaloxybicycloheptene (Id) gave 0.6 g of recovered diene, and 1.9 g (45% of the theoretical) of 1,4,5,8-diendomethylene-2- $\beta$ -decaloxy-5,6,7,8,9,9-hexachloro-1,2,3,4,4a,5,8a-octahydronaphthalene (IVd), b. p. 184-185.5° ( $2 \cdot 10^{-2}$  mm). (IVd) appeared as a very viscous, thermally poorly stable compound. Found: C 50.73, 50.81; H 4.80, 4.77%.  $C_{17}H_{20}Cl_6O$ . Calculated: C 50.84; H 4.55%.

\*The condensation of vinyl phenyl sulfide and vinyl ethyl sulfide with cyclopentadiene was carried out by us earlier [2] with equimolecular amounts of the starting materials. To compare the diene activity of vinyl ethers and thioethers, we give the results of experiments carried out with a two-fold excess of sulfide.




## Hydrogenation of the Adducts of the Diene Synthesis

A hydrogenation flask was charged with 4.6 g of 2-cyclohexoxybicyclo-(2,2,1)hept-5-ene (Ic) in 20 ml of methanol. Hydrogenation was carried out over platinum oxide prepared according to Adams, or over Raney nickel. Absorption of hydrogen occurred rapidly at room temperature (417 ml of hydrogen were required; volume actually absorbed, 398 ml). The yield of 2-cyclohexoxynorcamphane thus obtained was 4.2 g (89% of the theoretical). Data concerning the hydrogenation of the substances under study are given in Table 4.

TABLE 3. Raman Spectra

| Compound   | (VIa)      | (Va)       | (Ic)       | (Ib)       | (Ie)       | (IIb)      | (Ie)     |          |
|--|------------|------------|------------|------------|------------|------------|----------|----------|
|  |            |            |            |            |            |            | endo     | exo-     |
| Frequencies (cm <sup>-1</sup> ); intensities on a ten-point scale are indicated between brackets | 152 (2)    | 153 (3)    |            |            | 150 (1)    |            |          |          |
|  | 172 (2)    | 168 (2)    |            |            | 175 (1)    |            |          |          |
|  | 265 (0)    | 275 (2sh)  |            |            | 243 (2)    |            |          |          |
|  | 282 (0)    | 297 (2sh)  |            |            | 274 (2)    |            |          |          |
|  | 299 (1)    | 469 (1)    |            |            | 621 (2)    |            |          |          |
|  | 486 (0)    | 487 (0)    |            |            | 755 (2)    |            |          |          |
|  | 501 (0)    | 651 (0)    |            |            | 775 (0)    |            |          |          |
|  | 529 (1)    | 672 (4)    |            | 675 (0)    | 809 (4)    | 624 (0)    |          |          |
|  | 553 (0)    | 703 (2sh)  |            | 750 (1)    | 857 (0)    | 802 (0)    |          |          |
|  | 673 (4)    | 728 (0)    |            | 775 (0)    | 912 (2)    | 845 (0)    |          |          |
|  | 702 (2sh)  | 811 (1)    | 788 (0)    | 835 (1sh)  | 932 (0)    | 902 (1)    |          |          |
|  | 732 (0)    | 888 (1)    | 839 (1)    | 899 (2sh)  | 953 (1)    | 921 (4)    |          |          |
|  | 812 (1)    | 912 (2)    | 900 (1sh)  | 943 (2)    | 973 (0)    | 965 (2sh)  |          |          |
|  | 887 (2)    | 914 (4)    | 945 (1sh)  | 960 (0)    | 1002 (9)   | 1035 (3)   |          |          |
|  | 913 (2)    | 943 (0)    | 989 (0)    | 1020 (2)   | 1033 (4)   | 1102 (3 d) |          |          |
|  | 944 (3sh)  | 970 (0)    | 1023 (2)   | 1091 (4)   | 1054 (1)   | 1138 (1)   |          |          |
|  | 968 (0)    | 985 (0)    | 1043 (6)   | 1116 (0)   | 1102 (5)   | 1159 (0)   |          |          |
|  | 981 (0)    | 1003 (1)   | 1063 (0)   | 1238 (0)   | 1125 (0)   | 1190 (0)   |          |          |
|  | 1004 (1)   | 1051 (1)   | 1089 (2)   | 1265 (0)   | 1158 (3)   | 1244 (2)   |          |          |
|  | 1025 (0)   | 1068 (1)   | 1114 (0)   | 1289 (1)   | 1177 (1)   | 1302 (1)   |          |          |
|  | 1059 (1sh) | 1101 (5sh) | 1152 (0)   | 1375 (1)   | 1246 (2sh) | 1316 (1)   |          |          |
|  | 1102 (5sh) | 1140 (1)   | 1218 (0)   | 1444 (3 d) | 1304 (1sh) | 1354 (0)   |          |          |
|  | 1138 (1)   | 1163 (0)   | 1252 (0)   | 1567 (6)   | 1362 (0)   | 1388 (0)   |          |          |
|  | 1165 (0)   | 1189 (1)   | 1342 (0)   | 1615 (0)   | 1440 (0)   | 1478 (1)   | 1452 (0) | 1438 (0) |
|  | 1191 (0)   | 1289 (0)   | 1373 (1)   |            | 1460 (0)   | 1571 (4)   | 1489 (1) | 1452 (0) |
|  | 1288 (0)   | 1388 (0)   | 1437 (2sh) |            | 1521 (0)   | 1618 (2)   | 1509 (1) | 1520 (0) |
|  | 1382 (0)   | 1428 (0)   | 1566 (6)   |            | 1578 (6)   | 1657 (0)   | 1543 (1) |          |
|  | 1455 (3sh) | 1454 (1sh) | 1616 (0)   |            | 1608 (4)   |            | 1589 (2) | 1579 (4) |
|  | 1575 (6)   | 1576 (6)   |            |            |            |            | 1602 (0) | 1609 (1) |

TABLE 4. Description of the Hydrogenated Adducts of Vinyl Ethers with Cyclopentadiene

| Formula   | B.p., °C<br>(pressure<br>in mm) | n <sub>D</sub> <sup>20</sup> | d <sub>4</sub> <sup>20</sup> | MR    |       | Found, %       |                | Calc. % |       | Yield<br>(% of the<br>theoretical) |
|---|---------------------------------|------------------------------|------------------------------|-------|-------|----------------|----------------|---------|-------|------------------------------------|
|   |                                 |                              |                              | found | calc. | C              | H              | C       | H     |                                    |
|  OC <sub>6</sub> H <sub>11</sub> (cyclo) | 94 (3)                          | 1,4880                       | 0,9903                       | 56,74 | 67,24 | 80,46<br>80,64 | 11,32<br>11,46 | 80,32   | 11,48 | 89                                 |
|  OC <sub>10</sub> H <sub>17</sub> (s)    | 165 (2)                         | 1,5085                       | 1,0052                       | 73,13 | 73,55 | 82,38<br>82,42 | 10,90<br>10,72 | 82,19   | 11,30 | 88                                 |
|  OC <sub>6</sub> H <sub>11</sub>         | 145 (6)                         | 1,4907                       | 0,9892                       | 68,32 | 68,93 | 81,90<br>81,70 | 11,40<br>11,05 | 82,00   | 11,19 | 91                                 |

## Preparation of Trihydrotriazole Derivatives by Reaction with Phenylazide

A mixture of 1.9 g (0.01 mole) of 2-cyclohexoxybicyclo-(2,2,1)hept-5-ene (Ic) and 2.4 g (0.02 mole) of phenylazide was left to stand at room temperature for 3 days. The white crystalline precipitate thus obtained (1.4 g) was filtered off and washed with diethyl ether. The description of this product, and of other compounds similarly prepared is given in Table 5.

## Spectroscopic Study of the Adducts Obtained

Infrared spectra were obtained in the region of 700-2,000  $\text{cm}^{-1}$  with the help of a one-beam infrared spectrometer IKS-11. The accuracy of frequency measurements of absorption bands was  $\pm 5 + 10 \text{ cm}^{-1}$ . Raman spectra were recorded with the help of a three-prism spectrograph ISP-67 with a  $f = 500 \text{ mm}$  chamber. The accuracy of the frequency determinations of the Raman spectra lines was  $\pm 1 \text{ cm}^{-1}$ .

TABLE 5. Description of the Condensation Products of the Adducts with Phenylazide

| Starting bicycloheptene | M. p., ( $^{\circ}\text{C}$ ) of the dihydrotriazole derivative | N% in the dihydrotriazole derivative |            |
|-------------------------|---|--------------------------------------|------------|
|                         |   | found                                | calculated |
| (Ic)                    | 134—136 decomp.   | 13,45; 13,65                         | 13,49      |
| (VIa)                   | 165—168 decomp.   | 12,50; 12,65                         | 12,37      |
| (VI c)                  | 200—202 decomp.   | 10,93; 11,03                         | 10,85      |

## SUMMARY

1. The reactivity of vinyl ethers containing hydroaromatic radicals in the diene synthesis with cyclopentadiene and hexachlorocyclopentadiene was investigated. A comparison between the diene activity of vinyl ethers with radicals of different structures showed that vinyl aryl ethers are more reactive in diene synthesis than their hydroaromatic analogs.
2. Introduction of a heteroatom in the  $\alpha$ -position to the double bond leads to a considerable increase of the dienophile activity of vinyl derivatives in this reaction; in this respect, sulfur has a greater effect than oxygen.
3. The presence of a bicycloheptene structure in diene synthesis adducts of vinyl ethers with cyclopentadiene and hexachlorocyclopentadiene was confirmed by spectroscopic methods. In addition to the already known absorption bands, a new band was found in the region of 990-1010  $\text{cm}^{-1}$ ; it appears to be characteristic for the given structure. The splitting of the double bond frequencies in the Raman spectra is apparently due to the existence of sterically isomeric forms of the bicycloheptene ring.

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# STUDIES OF THE LACTONES AND LACTAMS

## REPORT 17. A STUDY OF THE DIENOPHILIC ACTIVITY OF N-VINYL LACTAMS

### AND THE VINYL ETHER OF N-( $\beta$ -HYDROXYETHYL)PYRROLIDONE

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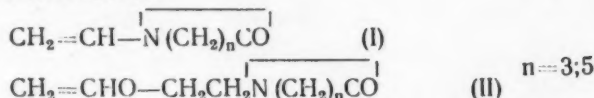
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No. 1, pp.128-135, January, 1961

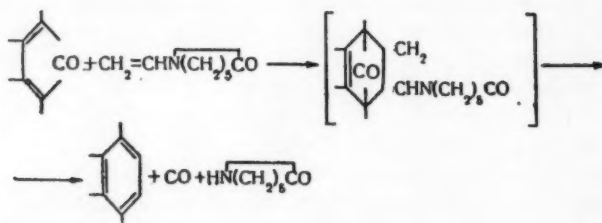
Original article submitted August 3, 1959

As was shown previously [1-4], the vinyl lactams (I) and the vinyl ether of N-( $\beta$ -hydroxyethyl)pyrrolidone (II) appear to be highly reactive substances and



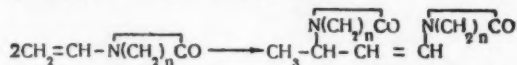
are able to take part in ionic and free radical reactions. In reactions that proceed by an ionic mechanism, however, the vinyl lactams show a number of peculiarities in comparison with unsubstituted vinyl ethers. The properties of the vinyl ether of N-( $\beta$ -hydroxyethyl)pyrrolidone (II) are similar to those both of the vinyl lactams and of the unsubstituted vinyl ethers. The properties of these compounds were studied previously in hydrolysis and polymerization reactions, in combination with hydrogen sulphide, etc. [3, 4]. It was considered of interest to study the behavior of vinyl lactams and vinyl ether (II) in diene synthesis reactions.

There is only one short reference to the use of vinyl lactams in diene synthesis. Abramov and Shapshinskaya [5], by reacting vinyl caprolactam and tetraphenylcyclopentadieneone separated out 1,2,3,4-tetraphenylbenzene and tar. On the basis of this the authors drew the conclusion that vinyl caprolactam reacts with substituted tetraphenylcyclopentadieneone in accordance with the usual scheme for vinyl compounds, i.e., with the splitting off of an endocarbonyl bridge.

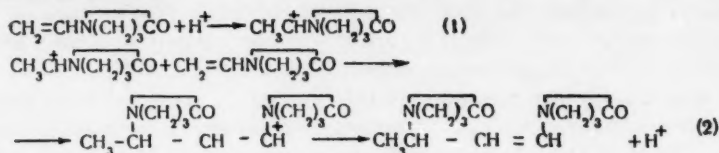


In the present research, the reactions of vinyl caprolactam and vinyl pyrrolidone with cyclopentadiene and hexachlorocyclopentadiene were studied. It was found that in the reaction of vinyl caprolactam and vinyl pyrrolidone with cyclopentadiene at 150-250° the diene condensation does not take place. Under these conditions, in the temperature range 140-180°, vinyl caprolactam and cyclopentadiene form a co-polymer in a small yield. Under the same conditions vinyl pyrrolidone, which has a tendency toward thermal polymerization, polymerizes with itself. With both compounds, under more severe conditions (240-250°), the formation of insoluble solid polymeric products which apparently had three dimensional structure was observed.

Interesting data were obtained from the study of the reaction of vinyl lactams with hexachlorocyclopentadiene. As in the case of cyclopentadiene, vinyl lactams did not give adducts with hexachlorocyclopentadiene; however, in a medium of this diene the vinyl lactams easily formed dimers.



The dimer of vinyl pyrrolidone was obtained by Breitenbach and his co-workers [6] by passing small quantities of gaseous hydrogen chloride through vinyl pyrrolidone. The authors [6] proved the structure of the dimer and proposed a mechanism for its formation.



It is probable that an analogous reaction mechanism occurs in the dimerization of vinyl lactams in a medium of hexachlorocyclopentadiene as a result of small quantities of hydrogen chloride which are given off.

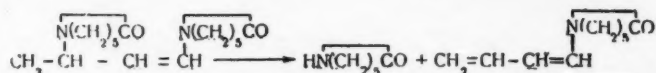
The constants, solubility, and ultraviolet spectrum (Fig. 2) of the dimer of vinyl pyrrolidone which we obtained coincided completely with those of the dimer described in the literature [6]. For the sake of comparison this product was synthesized by the regular method [6], i.e., by passing a small quantity of hydrogen chloride through vinyl pyrrolidone. The products obtained by the two methods were identical.

By extending these reactions to vinyl caprolactams, analogous results were obtained. Both in a hexachlorocyclopentadiene medium, and when small quantities of hydrogen chloride are passed through, the dimer of vinyl caprolactam is formed. The dimers of caprolactams are crystalline substances, insoluble in water. It should be noted that the crystallization of a dimer of vinyl pyrrolidone takes place extremely slowly. Even when the sample is kept in a refrigerator, the process does not reach a significant degree of completeness for two to three months, which greatly complicates work with the dimer of vinyl pyrrolidone. Crystallization of the dimer of vinyl caprolactam occurs much more rapidly and is complete in three to four days. This difference may be explained by the difference in size of the lactam ring.

Spectroscopic study of the dimers gave the following information: 1) the ultraviolet spectrum of the dimer of vinyl caprolactam (Fig. 1) is similar to the UV spectrum of the dimer of vinyl pyrrolidone (Fig. 2); 2) as in the case of the dimer of vinyl pyrrolidone, the UV spectrum of the dimer of vinyl caprolactam is similar to the spectrum of the original vinyl caprolactam. An intensive maximum absorption band exists at  $\lambda \sim 250 \text{ m}\mu$ , which is caused by the preservation of a double bond immediately adjacent to the lactam ring.

It is interesting to note that the dimerization of vinyl lactams in a medium of hexachlorocyclopentadiene gives the best yield (up to 75%) at room temperature. At 55-60° the yield of dimers decreases because of the appearance of tarry substances, while at temperatures above 100°, the dimer is not obtained at all, the main reaction product being a tar, with insignificant quantities (0.1-0.2 g) of a crystalline chlorohydrate of the respective lactams.

Study of the properties of the dimers of vinyl lactams showed that these substances are unstable at high temperatures. Thus, on heating the dimer of vinyl caprolactam for 2 hr at 200°, it decomposes yielding caprolactam and tar (under these conditions 60% decomposes). The nature of the tarry residue was not determined definitively, but its basic composition most nearly corresponds to the polymer of 1,4-butadiene-N-caprolactam, containing an atom of oxygen on one link of the chain (because of oxidation by the oxygen of the air). The decomposition of the dimer of vinyl caprolactam apparently occurs in accordance with the following scheme:



The thermal instability of the dimers appears to be the reason for the decrease in yield of these products at higher temperatures in the reaction of vinyl lactams with hexachlorocyclopentadiene. The lactams formed under these conditions react with hydrogen chloride existing in the system, giving the above mentioned chlorohydrates.

The fact that vinyl lactams form dimers in the hexachlorocyclopentadiene medium, which was found in this study, is interesting and completely unexpected. It is well known that simple unsubstituted vinyl ethers in the presence of hydrogen chloride easily yield polymers, products of hydrolysis, etc. [7]. At the same time, one of us with his co-workers [8] has shown that vinylalkyl, vinylaryl, and thio ethers on reacting with hexachlorocyclopentadiene undergo diene condensation and form adducts with good yields. Acetals and tarry substances were formed only as by-products. However, the authors [8] carried out the process at higher temperatures (100° and above). From the

literature it is also known that diene condensation of hexachlorocyclopentadiene with the majority of dienophils occurs in the temperature range from 70-200° [9]. There are only rare cases where this synthesis has been carried out at lower temperatures [10]. In this connection it still remains unclear whether the difference in the direction of the reaction of hexachlorocyclopentadiene with vinyl ethers, on the one hand, and vinyl lactams, on the other, results from the influence of the structure of the materials studied, or on the temperature of the reaction. For the sake of comparison we studied the reaction of hexachlorocyclopentadiene with a series of representative vinyl ethers at room temperature. It appears that unsubstituted vinylalkyl ethers (vinylethyl, vinylisopropyl, vinylbutyl, vinylphenyl-) undergo diene condensation with hexachlorocyclopentadiene even at room temperature, giving as adducts a series of bicycloheptenes with a yield of 60-80%. In numerous cases the formation of adducts was not accompanied by side reactions (acetal formation, tar formation). We believe that not only the vinyl, but also the thio ethers, as extremely active dienophils, may have the ability to undergo diene condensation with hexachlorocyclopentadiene at lower temperatures.

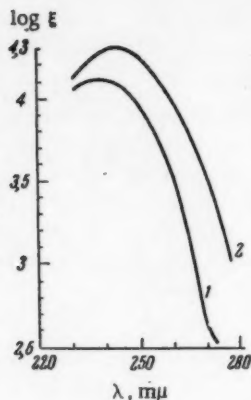


Fig. 1. The UV spectra of vinyl caprolactam and the dimer of vinyl caprolactam in alcohol: 1) vinyl caprolactam; 2) dimer of vinyl caprolactam.

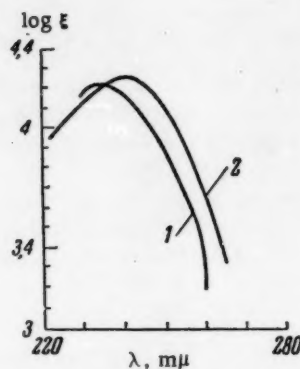
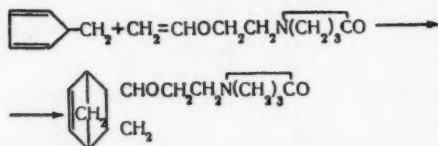
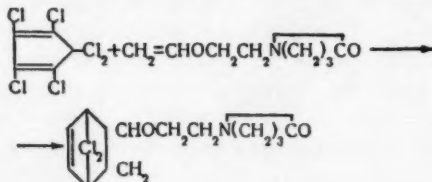


Fig. 2. The UV spectra of vinyl pyrrolidone and the dimer of vinyl pyrrolidone in alcohol: 1) vinyl pyrrolidone; 2) dimer of vinyl pyrrolidone.

As was previously mentioned, the vinyl ether of  $\beta$ -hydroxyethylpyrrolidone closely resembles the vinylalkyl ethers in its ability to react. As a matter of fact, in carrying out the diene condensation of the vinyl ether of  $\beta$ -hydroxyethylpyrrolidone with cyclopentadiene and hexachlorocyclopentadiene, and in the case of unsubstituted vinyl ethers as well, the corresponding adducts were obtained. By reaction with cyclopentadiene 2- $\beta$ -(N-pyrrolidonyl)-ethoxy-bicyclo-(2,2,1)-heptene-5 was obtained; yield, 32%:



Analogously, using hexachlorocyclopentadiene, 1,4,5,6,7,7-hexachloro-2- $\beta$ -(N-pyrrolidonyl)ethoxy-bicyclo-(2,2,1)-heptene-5 was obtained. The yield of the latter when the reaction was carried out at 100° was 80%; at room temperature the yield was only 37%.



The dimer of the vinyl ether of  $\beta$ -hydroxyethylpyrrolidone was not found after reaction with hexachlorocyclopentadiene. Neither was the dimer observed on passing dry hydrogen chloride through this vinyl ether.

This study has shown that in reactions with such dienes as cyclopentadiene and hexachlorocyclopentadiene, the behavior of the vinyl ethers and the vinyl lactams varies. The properties of the vinyl ether of  $\beta$ -hydroxyethylpyrrolidone, as a compound in which the lactam ring is not directly linked to a double bond but is a substituent in an alkyl radical, are closer to the properties of unsubstituted vinyl ethers.

#### EXPERIMENTAL\*

The reaction of vinyl caprolactam with cyclopentadiene. 14 g (0.1 M) of freshly distilled vinyl caprolactam and 3.5 g (0.05 M) of freshly distilled cyclopentadiene were heated in an autoclave for 16 hr at 180–190°. 1.2 g of a cyclopentadiene polymer with a softening temperature of 140–150° was separated from the reaction mixture. By fractionation of the residue, the following were obtained: 10.1 g of vinyl caprolactam, 1.1 g of caprolactam (a mixed melting point with a sample gave no depression) and 3.8 g of a tarry residue. By reprecipitating the latter from a benzene solution by means of petroleum ether (b. p. 35–50°), 0.65 g of a light-brown powder were separated out which appeared to be the co-polymer of vinyl caprolactam and cyclopentadiene (yield 6% of the original mixture). Found: C 73.69, 73.78%; H 9.45, 9.56%; N 5.94, 5.76%; mol. wt. 369.3, 380 (determined cryoscopically in benzene). The composition of this substance was: vinyl caprolactam ~38 mole %, cyclopentadiene ~62 mole %.

The reaction of vinyl pyrrolidone with cyclopentadiene. From 11 g (0.1 M) of vinyl pyrrolidone and 3.5 g (0.05 M) of cyclopentadiene, under the same conditions as the previous experiment, we obtained: 7.3 g of vinyl pyrrolidone, 1.76 g of a polymer of cyclopentadiene, and 1.89 g of a polymer of vinyl pyrrolidone; after reprecipitation from acetone by means of ether we found: C 64.19, 63.94%; H 8.33, 8.20%.  $C_6H_9ON$ , calculated: C 64.86%; H 8.16%; N 12.60%.

TABLE 1. Reaction Conditions and Results of the Reaction of Vinyl Caprolactam (6.5 g; 0.04 M) with Hexachlorocyclopentadiene (5.42 g; 0.02 M)

| Reaction conditions |               | Yield of the dimer of vinyl caprolactam, % | Other reaction products   |
|---------------------|---------------|--|---|
| temperature °C      | time in hours |  |   |
| 18–20               | 120           | 76,4                                       | 5.0 g hexachlorocyclopentadiene<br>0.1 g of caprolactam chlorohydrate     |
| 55–60               | 6             | 65,2                                       | 5.0 g of hexachlorocyclopentadiene<br>0.11 g of caprolactam chlorohydrate |
| 95–100              | 6             | 3,9  | 0.3 g of caprolactam chlorohydrate<br>8.5 g of tar                        |
| 120*                | 0,25          | —  | The reaction mass was a black powder which gave off hydrogen chloride     |

\* The experiment was carried out in an autoclave. A jump in temperature to 230° was observed.

The reaction of the vinyl ether of  $\beta$ -hydroxyethylpyrrolidone with cyclopentadiene. 15.5 g (0.1 M) of the vinyl ether of  $\beta$ -hydroxyethylpyrrolidone and 3.3 g (0.05 M) of cyclopentadiene were heated for 27 hr in an autoclave at 180–190°. By fractionation of the reaction mixture we obtained 11.6 g of the original vinyl ether, fraction I with b. p. 85–99° ( $1 \cdot 10^{-2}$  mm) 1.3 g (an amorphous polymer of cyclopentadiene with softening point of 140–150°), and fraction II with b. p. 147–155° ( $9 \cdot 10^{-3}$  mm) (distills simultaneously with the polymer of cyclopentadiene). After

\* The UV spectra were taken under the direction of T. N. Shkurina in the spectroscopic laboratory.

filtering off the polymer we obtained 3.4 g (yield 32% of theoretical) of 2- $\beta$ -hydroxyethylpyrrolidonyl-bicyclo-(2,2,1)heptene-5 (a viscous light-yellow liquid  $n_D^{20}$  1.5155). Found: C 70.40, 70.10%; H 8.83, 8.80%; N 6.43, 6.07%.  $C_{13}H_{19}O_2N$ . Calculated: C 70.55%; H 8.65%; N 6.33%.

The reaction of vinyl caprolactam with hexachlorocyclopentadiene. The original hexachlorocyclopentadiene was purified chromatographically on silica gel and subsequently distilled (freezing point 10.7°). A mixture of 5.5 g (0.04 M) of vinyl caprolactam and 5.4 g (0.02 M) of hexachlorocyclopentadiene was maintained at room temperature. After 48 hr the formation of an amorphous precipitate was observed, which after five days filled the entire mass. The precipitate was separated and washed with petroleum ether and ether. From the filtrate were separated 5.0 g of hexachlorocyclopentadiene and 0.1 g of caprolactam chlorohydrate, m. p. 140-146° (a mixed melting point with a sample of caprolactam chlorohydrate showed no depression). The precipitate mentioned above (4.2 g, yield 76%) was a dimer of vinyl caprolactam with m. p. 142-143.5°. In order to purify it, to 0.2 g of the dimer in 2.5 ml of methanol was added 100 ml of petroleum ether and the solution placed in a refrigerator. After three days needle-like crystals of the dimer of vinyl caprolactam precipitated; m. p. 143-143.5° (a mixed melting point with the dimer of vinyl caprolactam, obtained from vinyl caprolactam by treatment with hydrogen chloride, showed no depression). The dimer is soluble in acetone, methanol, water, and carbon tetrachloride. Found: C 69.38, 69.23%; H 9.28, 9.44%; N 10.60, 10.49%. The substance does not contain chlorine.  $C_{16}H_{26}O_2N$ . Calculated: C 69.02%; H 9.41%; N 10.06%.

The remaining experiments on the reaction of vinyl caprolactam with hexachlorocyclopentadiene are shown in Table 1.

Formation of the dimer of vinyl caprolactam under the influence of hydrogen chloride. A current of dry hydrogen chloride was passed through a solution of 3.0 g of vinyl caprolactam in 3.5 ml of absolute ether for a period of 15 seconds. After some hours a white amorphous powder precipitated which was separated and washed with petroleum ether and then with ether. Weight 2.8 g (yield 93%); m. p. 142-143°.

Behavior of the dimer of vinyl caprolactam on heating. 4.2 g of the dimer of vinyl caprolactam was heated at 200° for 2 hr. No low boiling products were observed. The reaction mixture was dissolved in benzene and the original dimer of vinyl caprolactam (1.1 g), m. p. 142-143°, was precipitated out with petroleum ether; by distillation of the filtrate 1.06 g of caprolactam was obtained which represents 63% decomposition of the dimer originally used; b. p. 115-116° (3 mm), m. p. 67-68° (a mixed melting point with a sample of caprolactam showed no depression), and 1.6 g of a tarry residue. The latter was reprecipitated from a benzene solution by means of petroleum ether, which yielded 0.85 g of a light-brown powder; this, after further purification (reprecipitation twice from benzene solution by means of petroleum ether) had a m. p. 75-80°. Found: C 67.50, 67.67%; H 8.59, 8.80%; N 7.48%; O 16.2% (by difference).  $C_{10}H_{15}ON$ . Calculated: C 72.73%; H 9.15%; N 8.84%; O 0.64%.  $C_{10}H_{15}O_2N$ . Calculated: C 66.27%; H 8.34%; N 8.72%; O 17.6%. On decomposing the dimer of vinyl caprolactam in the presence of hydroquinone in an atmosphere of nitrogen caprolactam was also obtained as well as a tar, the composition of which was not studied.

The reaction of vinyl pyrrolidone with hexachlorocyclopentadiene at room temperature. Under the same conditions as with vinyl caprolactam, 4.4 g (0.04 M) of vinyl pyrrolidone and 5.4 g (0.02 M) of hexachlorocyclopentadiene were allowed to react and 4.07 g of the dimer of vinyl pyrrolidone were produced (yield 92%); b. p. 134-135° ( $1 \cdot 10^{-2}$  mm);  $n_D^{20}$  1.5410. On placing it in a refrigerator the dimer of vinyl pyrrolidone slowly crystallized (the melting point of a mixed sample with dimer obtained by Breitenbach's method [6] showed no depression). The reaction of identical quantities of vinyl pyrrolidone and hexachlorocyclopentadiene at 100° gave 0.2 g of pyrrolidone chlorohydrate with m. p. 75-80° (a mixed melting point with a sample of pyrrolidone chlorohydrate showed no depression), and tar.

The reaction of the vinyl ether of  $\beta$ -hydroxyethylpyrrolidone with hexachlorocyclopentadiene. 7.5 g (0.05 M) of the vinyl ether of  $\beta$ -hydroxyethylpyrrolidone and 8.1 g (0.03 M) of hexachlorocyclopentadiene were heated with stirring for 2 hr. On fractionating the reaction mixture the following were obtained: 2.3 g of the original hexachlorocyclopentadiene, 2.4 g of vinyl ether, and 7.2 g of 1,4,5,6,7,7-hexachloro-2- $\beta$ -hydroxyethylpyrrolidonyl-bicyclo-(2,2,1)heptene-5, b. p. 152-155° ( $8 \cdot 10^{-3}$  mm);  $n_D^{20}$  1.5545 (the yield was 45.5% of theoretical or 80% based on the amount of diene entering the reaction). This is a light-yellow viscous liquid which is soluble in benzene and acetone, but not in water. Found: Cl 49.03, 48.58%; N 3.40, 3.47%.  $C_{13}H_{18}O_2Cl_6$ . Calculated: Cl 48.57%; N 3.20%. When this reaction was carried out at room temperature, 3.8 g (0.025 M) of the vinyl ether of  $\beta$ -hydroxyethylpyrrolidone and 4.65 g (0.015 M) of hexachlorocyclopentadiene yielded 1.41 g of an adduct (yield 17.7% of theoretical, or 37% on the basis of the diene entering the reaction), 3.2 g of hexachlorocyclopentadiene, and 1.7 g of vinyl ether.

The reaction of the vinyl ether of  $\beta$ -hydroxyethylpyrrolidone with hydrogen chloride. Hydrogen chloride was passed through the vinyl ether of  $\beta$ -hydroxyethylpyrrolidone in an experiment analogous to that with vinyl pyrrolidone [6]. On standing for a month at room temperature the reaction mixture took on a brown color. By precipitation with petroleum ether from a benzene solution, 0.48 g of tar were obtained. The remainder was distilled in vacuo and a fraction obtained with a b. p. 147-152° (4.5 mm);  $n_D^{20}$  1.4930, containing 32.03-32.80% of the vinyl ether of  $\beta$ -hydroxyethylpyrrolidone [2] (bisulphite method).

TABLE 2. Results of the Reaction of some Vinyl Ethers with Hexachlorocyclopentadiene

| Vinyl ether     | Yield of adduct, % |                         | B. p., °C<br>(mm Hg) | $n_D^{20}$ | Published data                                 |
|-----------------|--------------------|-------------------------|----------------------|------------|--|
|                 | of theoretical     | based on diene reacting |                      |            |  |
| Vinylethyl-     | 30                 | 63                      | 133-135 (5)          | 1,5955     | B. p. 134-135° (5 mm)<br>$n_D^{20}$ 1,5358 [1] |
| Vinylbutyl-     | 41                 | 77                      | 139-140 (2)          | 1,5245     | B. p. 140-141° (2 mm)<br>$n_D^{20}$ 1,5250 [8] |
| Vinylisopropyl- | 16                 | 52                      | 118-120<br>(2,5)     | 1,5259     | —  |
| Vinylphenyl-    | 4                  | 55                      | 162-163<br>(2,5)     | 1,5715     | B. p. 161° (3 mm) [8]                          |

The reaction of vinylethyl, vinylisopropyl, vinylisobutyl, and vinylphenyl ethers with hexachlorocyclopentadiene. We shall describe one of the experiments as an example. A mixture of 3.44 g (0.04 M) of vinylisopropyl ether and 5.3 g (0.02 M) of hexachlorocyclopentadiene was kept for 15 days at room temperature. Then the vinylisopropyl ether was distilled off at the same temperature in vacuo, after which the mixture was fractionated, yielding: 3.8 g of hexachlorocyclopentadiene and 1.15 g (yield 16% of theoretical or 52% based on the amount of diene entering the reaction) of 1,4,5,6,7,7-hexachloro-2-isopropoxy-bicyclo-(2,2,1)heptene-5 with b. p. 118-120° (2.5 mm);  $n_D^{20}$  1.5259. Found: C 32.98, 32.97%; H 2.52, 2.56%; Cl 59.38, 59.62%.  $C_{16}H_{10}OCl_6$ . Calculated: C 33.46%; H 2.88%; Cl 59.28%.

The adducts of some vinyl ethers and hexachlorocyclopentadiene were synthesized under these conditions. The results obtained are shown in Table 2.

#### SUMMARY

1. The dienophilic activity of vinyl lactams was studied, using as examples the reaction of vinyl pyrrolidone and vinyl caprolactam with cyclopentadiene and hexachlorocyclopentadiene. Under the conditions studied, vinyl lactams do not undergo diene condensation with the dienes mentioned.
2. In a hexachlorocyclopentadiene medium, the vinyl lactams form dimers.
3. Unsubstituted vinylalkyl and vinylaryl ethers and the vinyl ether of  $\beta$ -hydroxyethylpyrrolidone are able to undergo diene condensation with hexachlorocyclopentadiene at room temperature.
4. In the reaction of the vinyl ether of  $\beta$ -hydroxyethylpyrrolidone with cyclopentadiene and hexachlorocyclopentadiene, the corresponding adducts of a series of bicycloheptenes were obtained.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

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## SYNTHESIS OF SATURATED PRIMARY-SECONDARY $\gamma$ -GLYCOLS

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Quite a large number of  $\gamma$ -glycols of different structures have now been described in the literature. The most widely known are diprimary, disecundary, and ditertiary  $\gamma$ -glycols, which are obtained by reduction of substituted succinic acids [1], condensation of acetylene with aldehydes and ketones [2] (by Iotsich's method) with subsequent hydrogenation of the acetylenic glycols, reaction of succinic ester with organomagnesium compounds [3], and other methods. At the same time, one only encounters isolated descriptions of unsymmetrical primary-secondary  $\gamma$ -glycols in the literature [4, 5, 6].

In several examples, we showed previously [7, 8] that it is possible to prepare primary-secondary  $\gamma$ -glycols by reduction of ethyl esters of  $\gamma$ -keto acids with lithium aluminum hydride. Continuing this work, we came to the conclusion that primary-secondary  $\gamma$ -glycols of various structures are readily obtained by this method. We prepared [8, 9] the  $\gamma$ -keto acids, which are required for this purpose in the form of their ethyl esters, by the known isomeric conversion of alkyl(aryl)furylcarbinols in an acid medium [10]. In addition, some aryl  $\gamma$ -keto acids were obtained by condensation of succinic anhydride with aromatic hydrocarbons by the Friedel-Crafts method [11, 12, 13, 14].

The  $\gamma$ -keto acids or their ethyl esters were reduced with a twofold excess of lithium aluminum hydride in absolute ether. The  $\gamma$ -glycols, which were obtained in 70-98% yield, were either thick, colorless liquids or white, crystalline substances, that were quite difficultly soluble in ether and readily soluble in acetone and alcohol. When heated with dilute sulfuric acid, the glycols readily lost water with the formation of the corresponding alkyl(aryl)-tetrahydrofurans, which were colorless, mobile liquids with a pleasant odor.

### EXPERIMENTAL

#### Preparation of Primary-Secondary $\gamma$ -Glycols

1,4-Pentanediol [4]. With continuous stirring, a solution of 150 g (1.04 mole) of ethyl levulinate in 120 ml of absolute ether was added to a solution of 40 g (1.05 mole) of lithium aluminum hydride in 1300 ml of absolute ether at such a rate that the ether boiled steadily. The reaction mixture was then boiled for 2-3 hr and the lithium complex formed was decomposed by the successive addition of 30 ml of water and 400 ml of 20% sulfuric acid solution. The glycol was extracted with ether with a small amount of acetone added, the residual aqueous solution neutralized and evaporated to dryness, and a further amount of glycol extracted from the solid residue with a mixture of ether and acetone. The combined extracts were washed with saturated potassium carbonate solution and dried over baked potassium carbonate. After removal of the solvent, the glycol was vacuum distilled. We obtained 76 g of 1,4-pentanediol (70% yield) with b. p. 121-122° at 12 mm;  $n_D^{20}$  1.4480;  $d_4^{20}$  0.9836; found  $MR_D$  28.34; calculated  $MR$  28.30. Found: C 57.20, 57.27; H 11.89, 11.68%.  $C_5H_{12}O_2$ . Calculated: C 57.65; H 11.51%.

1,4-Hexanediol [5] was obtained analogously by reduction of 115 g (0.7 mole) of ethyl 4-ketohexanoate [10] with 26.6 g (0.7 mole) of lithium aluminum hydride in 1200 ml of absolute ether. After decomposition of the complex with 50 ml of water and 300 ml of 20% sulfuric acid, the glycol was extracted with a mixture of ether and acetone. The extract was washed with saturated potassium carbonate solution and dried over baked potassium carbonate. Removal of the solvent and vacuum distillation of the glycol yielded 59 g of 1,4-hexanediol (68% yield) with b. p. 101-102° (2 mm);  $n_D^{20}$  1.4540;  $d_4^{20}$  0.9756; found  $MR_D$  32.80, calculated  $MR$  32.96. Found: C 60.59, 60.88; H 11.74, 11.87%.  $C_6H_{14}O_2$ . Calculated: C 60.98; H 11.94%.

1,4-Heptanediol [6, 8] was obtained analogously by reduction of 265 g (1.5 mole) of ethyl 4-ketoheptanoate [8, 10] with 57 g (1.5 mole) of lithium aluminum hydride in 1400 ml of absolute ether in 72% yield. The glycol was a thick, colorless liquid with b. p. 112-115° (3 mm);  $n_D^{20}$  1.4523;  $d_4^{20}$  0.9526; found  $MR_D$  37.46; calculated  $MR$  37.58. Found: C 63.86, 63.50; H 12.70, 12.59%.  $C_7H_{16}O_2$ . Calculated: C 63.59; H 12.19%.

6-Methyl-1,4-heptanediol [8] was obtained analogously from 186 g (1 mole) of ethyl 6-methyl-4-ketoheptanoate [9, 10] and 38 g (1 mole) of lithium aluminum hydride in 1200 ml of absolute ether with the only difference that the complex was decomposed by the addition of 350 ml of iced water. Removal of the solvent and vacuum distillation of the product yielded 124 g (85%) of the glycol with b. p. 126-127° (7 mm);  $n_D^{20}$  1.4512;  $d_4^{20}$  0.9361; found MR<sub>D</sub> 42.08; calculated MR 42.19. Found: C 65.46; H 12.18%.  $C_8H_{18}O_2$ . Calculated: C 65.70; H 12.40%.

6,6-Dimethyl-1,4-heptanediol was obtained analogously by reduction of 70.4 g of ethyl 6,6-dimethyl-4-ketoheptanoate [9, 10] with 14 g of lithium aluminum hydride in 600 ml of absolute ether. The yield was 85%. The glycol was a thick, colorless liquid with b. p. 112-114° (3 mm);  $n_D^{20}$  1.4545;  $d_4^{20}$  0.9319; found MR<sub>D</sub> 46.61; calculated MR 46.81. Found: C 67.50, 67.44; H 12.34, 12.47%.  $C_9H_{20}O_2$ . Calculated: C 67.45; H 12.58%.

1,4-Octanediol [8]. Analogously, from 197 g of ethyl 4-ketooctanoate [9] and 40 g of lithium aluminum hydride in 1200 ml of absolute ether we obtained 140 g (89.6%) of 1,4-octanediol with b. p. 116-117° (3 mm);  $n_D^{20}$  1.4540;  $d_4^{20}$  0.9386; found MR<sub>D</sub> 42.19; calculated MR 42.19. Found: C 65.40, 65.51; H 12.37, 12.84%.  $C_8H_{18}O_2$ . Calculated: C 65.70; H 12.40%.

6-Methyl-1,4-octanediol [8] was obtained analogously by reduction of 238 g of ethyl 6-methyl-4-ketooctanoate [8] with 47 g of lithium aluminum hydride in 1500 ml of absolute ether. The product (154 g, 81%) had b. p. 117-118° (4 mm);  $n_D^{20}$  1.4558;  $d_4^{20}$  0.9320; found MR<sub>D</sub> 46.72; calculated MR 46.81. Found: C 67.60; H 12.12%.  $C_9H_{20}O_2$ . Calculated: C 67.45; H 12.58%.

7-Methyl-1,4-octanediol [8]. The reduction of 98 g (0.5 mole) of ethyl 7-methyl-4-ketooctanoate [9, 10] with 19 g (0.5 mole) of lithium aluminum hydride in 700 ml of absolute ether yielded 65 g (83%) of 7-methyl-1,4-octanediol with b. p. 127-129° (4 mm);  $n_D^{20}$  1.4530;  $d_4^{20}$  0.9262; found MR 46.69; calculated MR 46.81. Found: C 67.88, 67.55; H 12.56, 12.81%.  $C_9H_{20}O_2$ . Calculated: C 67.45; H 12.58%.

6,6-Dimethyl-1,4-octanediol was obtained analogously from 76 g of ethyl 6,6-dimethyl-4-ketooctanoate [9] and 14 g of lithium aluminum hydride in 700 ml of absolute ether. The product (56 g, 91%) had b. p. 123-124° (3 mm);  $n_D^{20}$  1.4637;  $d_4^{20}$  0.9373; found MR 51.28; calculated MR 51.43. Found: C 68.89, 68.79; H 12.81, 12.71%.  $C_{10}H_{22}O_2$ . Calculated: C 68.92; H 12.72%.

1,4-Nonanediol [8] was obtained analogously by reduction of 202 g of ethyl 4-ketononanoate [9, 10] with 38 g of lithium aluminum hydride in 1400 ml of absolute ether. The glycol (70% yield) was a colorless liquid with b. p. 136-138° (5 mm);  $n_D^{20}$  1.4549;  $d_4^{20}$  0.9292; found MR 46.78; calculated MR 46.81. Found: C 67.60; H 12.62%.  $C_9H_{20}O_2$ . Calculated: C 67.45; H 12.58%.

8-Methyl-1,4-nonanediol [8] was obtained analogously in 84% yield from 107 g of ethyl 8-methyl-4-ketononanoate [9] and 19 g of lithium aluminum hydride in 700 ml of absolute ether. The glycol was a thick, colorless liquid with b. p. 132-133° (3 mm);  $n_D^{20}$  1.4543;  $d_4^{20}$  0.9189; found MR 51.39; calculated MR 51.43. Found: C 68.54; H 12.77%.  $C_{10}H_{22}O_2$ . Calculated: C 68.91; H 12.72%.

1,4-Decanediol [6] was obtained analogously in 92% yield by reduction of 260 g of ethyl 4-ketodecanoate [9] with 46 g of lithium aluminum hydride in 1500 ml of absolute ether and had b. p. 139-140° (3 mm);  $n_D^{20}$  1.4558;  $d_4^{20}$  0.9249; found MR 51.20; calculated MR 51.43. The glycol crystallized on standing and had m. p. 26-27°; found: C 69.15, 69.07; H 12.79, 12.81%.  $C_{10}H_{22}O_2$ . Calculated: C 68.92; H 12.72%.

1,4-Dodecanediol was obtained in 95% yield by reduction of 189 g of ethyl 4-ketododecanoate [9] with 30 g of lithium aluminum hydride in 220 ml of absolute ether. The glycol was a crystalline substance with m. p. 46-46.5°. Found: C 71.40, 71.31; H 13.15, 13.17%.  $C_{12}H_{26}O_2$ . Calculated: C 71.23; H 12.95%.

6-Methyl-1,4-dodecanediol [8] was obtained analogously from 128 g (0.5 mole) of ethyl 6-methyl-4-ketododecanoate [9] and 19 g (0.5 mole) of lithium aluminum hydride in 1000 ml of absolute ether. The yield was 90%. The glycol was a white, crystalline powder with m. p. 49-50°. Found: C 72.02; H 12.95%.  $C_{13}H_{28}O_2$ . Calculated: C 72.16; H 13.04%.

1,4-Tridecanediol was obtained analogously from 180 g of ethyl 4-ketotridecanoate [9] and 27 g of lithium aluminum hydride in 1600 ml of absolute ether. After vacuum distillation, the glycol crystallized and had m. p. 42.5-43° (89% yield). Found: C 71.89, 71.85; H 12.87, 12.65%.  $C_{13}H_{28}O_2$ . Calculated: C 72.16; H 13.04%.

1,4-Pentadecanediol. Reduction of 65 g of ethyl 4-ketopentadecanoate [9] with 9 g of lithium aluminum hydride in 500 ml of absolute ether as above yielded 42 g of 1,4-pentadecanediol as white crystals with m. p. 59-60°. Found: C 73.65, 73.76; H 13.35, 13.32%.  $C_{15}H_{32}O_2$ . Calculated: C 73.71; H 13.19%.

5-Cyclohexyl-1,4-pentanediol was obtained in 95.5% yield by reduction of 82 g of ethyl 6-cyclohexyllevulinate [10] with 14 g of lithium aluminum hydride in 400 ml of absolute ether by the procedure described above. The glycol crystallized after removal of the solvent. After recrystallization from ether, the 5-cyclohexyl-1,4-pentanediol melted at 59.5-60°. Found: C 71.12, 71.09; H 12.15, 12.20%.  $C_{11}H_{22}O_2$ . Calculated: C 70.92; H 11.91%.

4-Phenyl-1,4-butanediol [6]. Into a flask fitted with a stirrer with a seal and a Soxhlet extractor was placed a solution of 38 g (1 mole) of lithium aluminum hydride in 360 ml of absolute ether. Into the extractor was placed 120 g (0.67 mole) of  $\beta$ -benzoylpropionic acid [11] and the reaction mixture boiled until the latter dissolved completely. The normal treatment yielded 108 g of 4-phenyl-1,4-butanediol, which melted at 67-68° after recrystallization from ether. Found: C 72.66, 72.60; H 8.61, 8.51%.  $C_{10}H_{14}O_2$ . Calculated: C 72.30; H 8.43%.

4-(2'-Thienyl)-1,4-butanediol was obtained analogously from 37 g of  $\beta$ -(2'-thenoyl)propionic acid [12] and 8 g of lithium aluminum hydride in 400 ml of absolute ether and had m. p. 46-48° (from ether); the yield was 86%. Found: C 56.00; H 7.08%.  $C_8H_{12}O_2S$ . Calculated: C 55.78; H 7.02%.

6-Phenyl-1,4-hexanediol [8] was obtained as above in 87% yield by reduction of 6 g of 6-phenyl-4-ketohexanoic acid [8] with 1.6 g of lithium aluminum hydride in 200 ml of absolute ether. On recrystallization from ether, the glycol formed a white, crystalline substance with m. p. 58°. Found: C 74.06, 74.04; H 9.56, 9.38%.  $C_{12}H_{18}O_2$ . Calculated: C 73.86; H 9.73%.

7-Phenyl-1,4-heptanediol [8] was obtained in 95% yield by reduction of 360 g of ethyl 7-phenyl-4-ketohexanoate [9, 10] with 57 g of lithium aluminum hydride in 1900 ml of absolute ether by the procedure described above. After vacuum distillation (b. p. 175-177° at 3 mm), the glycol crystallized and had m. p. 43-44°. Found: C 74.61, 74.50; H 9.79, 9.65%.  $C_{12}H_{20}O_2$ . Calculated: C 74.96; H 9.68%.

4-(4'-Diphenyl)-1,4-butanediol was obtained by the addition of 77 g (0.32 mole) of  $\beta$ -(4-phenylbenzoyl)propionic acid [13] (as a suspension in ether) to a solution of 19 g (0.5 mole) of lithium aluminum hydride in 1000 ml of absolute ether with vigorous stirring. The normal treatment gave the glycol as a white, crystalline powder in 98% yield. After recrystallization from ether, the 4-(4'-diphenyl)-1,4-butanediol melted at 80°. Found: C 79.33, 79.24; H 7.19, 7.20%.  $C_{16}H_{18}O_2$ . Calculated: C 79.30; H 7.49%.

4-(2'-Naphthyl)-1,4-butanediol was obtained in 98% yield analogously by reduction of 36 g of  $\beta$ -(2-naphthyl)propionic acid [14] with 9 g of lithium aluminum hydride in 500 ml of absolute ether. The glycol was a white, crystalline substance with m. p. 88-89°, which dissolved readily in acetone and alcohol and less readily in ether. Found: C 77.65, 77.84; H 7.74, 7.60%.  $C_{14}H_{16}O_2$ . Calculated: C 77.74; H 7.45%.

3,4-Dimethyl-2,5-hexanediol. The reduction of 57 g of 3,4-dimethyl-2,5-hexanedione, which was obtained by Moore's method [15], with 16 g of lithium aluminum hydride in 500 ml of absolute ether gave a 90% yield of 3,4-dimethyl-2,5-hexanediol with b. p. 99-101° (2 mm);  $n_D^{20}$  1.4598;  $d_4^{20}$  0.9505; found MR 42.12; calculated MR 42.19. Found: C 65.63, 65.42; H 12.48, 12.58%.  $C_8H_{18}O_2$ . Calculated: C 65.70; H 12.41%.

#### Dehydration of some $\gamma$ -Glycols

$\alpha$ -(2-Methylbutyl)tetrahydrofuran. To 9.3 g of 7-methyl-1,4-octanediol was added 30 ml of 60-66% sulfuric acid solution, the mixture heated on a boiling water bath for an hour and then diluted with water, and the product steam distilled. The distillate (~200-250 ml) was saturated with potassium carbonate and extracted with ether and the extract dried over calcium chloride. After removal of the ether, the product was distilled over sodium. We obtained 4.7 g of pure  $\alpha$ -(2-methylbutyl)tetrahydrofuran with b. p. 172.5-173.5° (764 mm);  $n_D^{20}$  1.4303;  $d_4^{20}$  0.8475; found MR 43.36; calculated MR 43.20. Found: C 75.53; H 12.90%.  $C_9H_{18}O$ . Calculated: C 75.98; H 12.74%.

$\alpha$ -(3-Methylbutyl)tetrahydrofuran. Analogously, from 4.6 g of 6-methyl-1,4-octanediol we obtained 2.4 g  $\alpha$ -(3-methylbutyl)tetrahydrofuran with b. p. 172-173° (764 mm);  $n_D^{20}$  1.4330;  $d_4^{20}$  0.8550; found MR 43.23; calculated MR 43.20. Found: C 76.15; H 12.80%.  $C_9H_{18}O$ . Calculated: C 75.98; H 12.74%.

$\alpha$ -(2,2-Dimethylpropyl)tetrahydrofuran was prepared as above from 6,6-dimethyl-1,4-heptanediol and had b. p. 162.5-163.5° (764 mm) (after distillation over sodium);  $n_D^{20}$  1.4317;  $d_4^{20}$  0.8520; found MR 43.25; calculated MR 43.20. Found: C 75.65, 75.60; H 12.89, 12.77%.  $C_9H_{18}O$ . Calculated: C 75.98; H 12.74%.

$\alpha$ -Phenyltetrahydrofuran was obtained analogously by dehydration of 4-phenyl-1,4-butanediol and had b. p. 84-85° (5 mm);  $n_D^{20}$  1.5260;  $d_4^{20}$  1.0292; found MR 44.17; calculated MR 44.20. Found: C 81.00; H 8.10%.  $C_{10}H_{12}O$ . Calculated: C 81.04; H 8.16%.

$\alpha$ -(2-Thienyl)tetrahydrofuran. Heating 4-(2'-thienyl)-1,4-butanediol with dilute sulfuric acid yielded  $\alpha$ -(2-thienyl)tetrahydrofuran with b. p. 98-99° (5 mm);  $n_D^{20}$  1.5449;  $d_4^{20}$  1.1426; found MR 42.67; calculated MR 42.61. Found: C 62.15, 62.47; H 6.53, 6.62%.  $C_8H_{10}SO$ . Calculated: C 62.29; H 6.53%.

$\alpha$ -Tetrahydrofurylcyclohexylmethane (7.2 g, 72%) was obtained as above from 11 g of 5-cyclohexyl-1,4-pentanediol and had b. p. 230-231° (762 mm);  $n_D^{20}$  1.4690;  $d_4^{20}$  0.9295; found MR 50.41; calculated MR 50.24. Found: C 78.64, 78.68; H 12.07, 12.05%.  $C_{11}H_{20}O$ . Calculated: C 78.43; H 11.97%.

2,3,4,5-Tetramethyltetrahydrofuran was obtained by heating 3,4-dimethyl-2,5-hexanediol with dilute sulfuric acid. After distillation over sodium, the 2,3,4,5-tetramethyltetrahydrofuran had b. p. 136-137° (760 mm);  $n_D^{20}$  1.4213;  $d_4^{20}$  0.8415; found MR 38.65; calculated MR 38.47. Found: C 75.00, 74.81; H 12.90, 12.80%.  $C_8H_{16}O$ . Calculated: C 74.93; H 12.58%.

#### SUMMARY

1. A general method is proposed for the synthesis of saturated primary-secondary  $\gamma$ -glycols by reduction of  $\gamma$ -keto acids or their esters with lithium aluminum hydride. We prepared and characterized 23 primary-secondary  $\gamma$ -glycols, most of which have not been described in the literature.
2. The hydration of some of these with dilute sulfuric acid yielded the corresponding  $\alpha$ -alkyl(aryl)tetrahydrofurans.

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# REACTIONS OF CYCLOPENTADIENYLIDES

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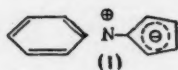
Translated from *Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk*,

No. 1, pp. 140-144, January, 1961

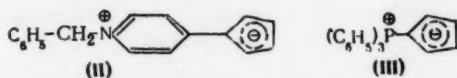
Original article submitted August 4, 1959

In an alkaline medium, cyclopentadiene is able to exchange all six hydrogen atoms for deuterium with deuterioethanol with exceptional ease [1]. This phenomenon has been explained by the intermediate formation of a stable cyclopentadienyl anion by the action of the base on cyclopentadiene. In agreement with this hypothesis, it was found that hydrogen exchange does not occur in neutral and weakly acid media.

It was to be expected that cyclopentadienylides, for example, pyridinium cyclopentadienylide (I),



whose molecule contains a negatively charged cyclopentadienylene residue, would not require the presence of alkali for hydrogen exchange, but would undergo this reaction even in neutral and weakly acid media. In actual fact it was found that cyclopentadienylides (pyridinium cyclopentadienylide (I) [2], N-benzylpyridinium  $\gamma$ -cyclopentadienylide (II) [3], and triphenylphosphonium cyclopentadienylide (III) [4]) react with deuterioethanol to exchange the hydrogen atoms for deuterium in alkaline, neutral, and weakly acid media.



The first act in this reaction is evidently the addition of a deuteron to the cyclopentadienyl anion, for example:



The second act consists of aromatic stabilization of the molecule with the elimination of a proton



Numerous repetitions of these acts leads to the exchange of hydrogen atoms for deuterium. It is possible that acts 1 and 2 overlap to some extent in time (are synchronized). If the reaction is carried out in a weakly acid medium, then act 1 is accelerated. If the reaction is carried out in an alkaline medium, then act 2 is accelerated. It is therefore probable that there was no substantial difference in the rates of the reactions in acid, neutral, and alkaline media under the conditions we investigated.

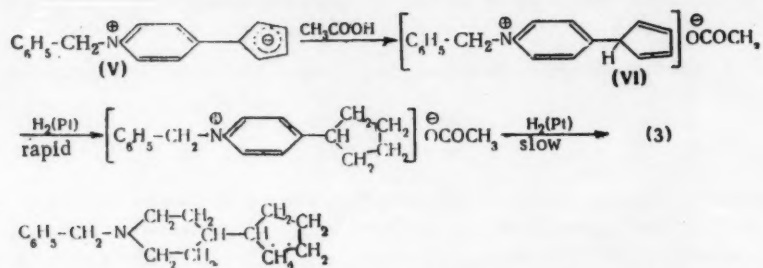
On the basis of the data we obtained on the deuterium exchange of cyclopentadiene and cyclopentadienylides, it could be surmised that in reactions of cyclopentadienylides with some other electrophilic reagents, all the hydrogen atoms of the negatively charged cyclopentadienylene residue should also be capable of undergoing substitution. In order to check this hypothesis, we studied the reaction of pyridinium cyclopentadienylide with an alkaline solution of potassium hypobromite.



In accordance with our expectations, as a result of the reaction we obtained a substance containing four bromine atoms in the cyclopentadienylene residue, namely, 1-pyridinium 2,3,4,5-tetrabromocyclopentadienylide (IV). This was an orange-red, crystalline substance, which dissolved in acids and precipitated from the solutions when alkali was added. It did not melt when heated to 200°, dissolved in polar solvents, and dissolved sparingly in nonpolar solvents. It gradually decomposed in air.

The exceptional stability of the negatively charged cyclopentadienylene group in cyclopentadienylides is also shown clearly by data on the catalytic hydrogenation of N-benzylpyridinium  $\gamma$ -cyclopentadienylide (V) in neutral and acid media. It was found that in the hydrogenation of N-benzylpyridinium  $\gamma$ -cyclopentadienylide [5] in ethanol, the absorption of hydrogen proceeds very slowly and at a gradually decreasing rate (graph, curve 1). In glacial acetic acid there is rapid absorption of the first two moles of hydrogen and then the hydrogenation rate falls rapidly (curve 2).

The probable reason for the difference in the rates of hydrogenation of N-benzylpyridinium  $\gamma$ -cyclopentadiene in ethanol and glacial acetic acid is the different states of the substance hydrogenated in these solvents. The cyclopentadienyl anion adds a proton in acetic acid and is converted to the cyclopentadienyl residue (VI) that contains two double bonds, which are hydrogenated rapidly, and then there is slow hydrogenation of the pyridine ring.



In alcohol, N-benzylpyridinium  $\gamma$ -cyclopentadienyliide retains its bipolar structure and hydrogenation of the cyclopentadienyl anion and the pyridine ring occurs slowly, at approximately the same rate.

The data we obtained were then confirmed by the work of Balandin and Khidekel' [6], who hydrogenated pyridinium cyclopentadienylide and N-benzylpyridinium  $\gamma$ -cyclopentadienylide over a rhodium catalyst in ethanol and acetic acid.

## EXPERIMENTAL

Hydrogen exchange of cyclopentadienylides. Experimental conditions: 0,005 mole of the cyclopentadienylide was dissolved in 100 ml of deuterioethanol and boiled. The alcohol was then removed in vacuum and the cyclopentadienylide dried, recrystallized, and burned over copper oxide. The excess density of the water from combustion was measured by the float method. The results are given in Table 1.

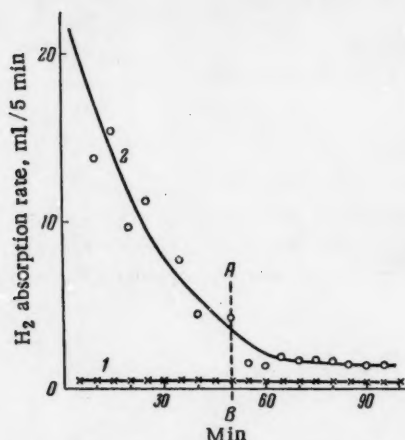
TABLE 1

| Cyclopentadienylide                                   | Reaction time, hr | Catalyst or pH of medium | Exchange as % of calculated |
|---|-------------------|--------------------------|-----------------------------|
| Pyridinium cyclopentadienylide (I)                    | 2                 | Without catalyst         | 47                          |
| » »   | 4                 | » »                      | 70                          |
| » »   | 6,5               | » »                      | 83                          |
| » »   | 5                 | pH 10,5                  | 64                          |
| Pyridinium cyclopentadienylide (I)                    | 4                 | 2,3 NaOH                 | 72                          |
| » »   | 5                 | pH 6,6                   | 82                          |
| » »   | 4                 | pH 3,4                   | 61                          |
| N-benzylpyridinium $\gamma$ -cyclopentadienylide (II) | 5                 | Without catalyst         | 57                          |
| Triphenylphosphonium cyclopentadienylide (III)        | 6,5               | » »                      | 83                          |
|   | 2                 | » »                      | 75                          |

Preparation of 1-pyridinium 2,3,4,5-tetrabromocyclopentadienyliide. An alkaline solution of potassium hypobromite, prepared by adding 4.33 g (0.0027 mole) of bromine to aqueous potassium hydroxide solution (8 g of KOH

in 34 ml of H<sub>2</sub>O) was added dropwise with vigorous stirring to a solution of 0.66 g (0.0046 mole) of pyridinium cyclopentadienylide in 150 ml of freshly distilled, dry chloroform. The pyridinium cyclopentadienylide was brominated

under conditions close to those for the bromination of cyclopentadiene in an alkaline medium [7]. The reaction mixture was cooled so that the temperature in the reaction flask did not rise above +1°. After the addition of the brominating mixture, stirring was continued for a further 4 hr at room temperature. The chloroform layer was then separated from the aqueous layer and evaporated to dryness in vacuum. Recrystallization from benzene yielded lustrous, golden yellow crystals which gradually became orange; they did not melt when heated to 200°. The yield of the product was 22%, calculated on the pyridinium cyclopentadienylide taken for the reaction. Found: C 26.58, 26.75; H 1.15, 1.31; N 3.22, 3.50; Br 68.86, 68.78%. C<sub>10</sub>H<sub>5</sub>Br<sub>4</sub>. Calculated: C 26.18; H 1.10; N 3.07; Br 69.67%.



Relation of the rate of hydrogenation of N-benzylpyridinium  $\gamma$ -cyclopentadienylide to time: 1) in ethanol; 2) in glacial acetic acid. The area bound by curve 2 and the broken line AB corresponds to two moles of hydrogen absorbed during hydrogenation.

TABLE 2

| Solvent             | Sample, g | Amount of hydrogen, ml |                          |
|---------------------|-----------|------------------------|--------------------------|
|                     |           | absorbed               | calc. for 5 double bonds |
| Ethanol             | 0,5019    | 232                    | 241                      |
| Glacial acetic acid | 0,5631    | 259                    | 270                      |
|                     | 0,5167    | 231                    | 248                      |

Catalytic hydrogenation of N-benzylpyridinium  $\gamma$ -cyclopentadienylide. N-Benzylpyridinium  $\gamma$ -cyclopentadienylide was hydrogenated in a hydrogenation flask at room temperature over Pt-black in alcohol and in glacial acetic acid. The results are given in Table 2.

#### SUMMARY

1. Cyclopentadienylides undergo isotopic exchange of hydrogen with deuterioethanol in alkaline, neutral, and weakly acid media.

2. 1-Pyridinium 2,3,4,5-tetrabromocyclopentadienylide was obtained by bromination of pyridinium cyclopentadienylide in an alkaline medium.

3. N-Benzylpyridinium  $\gamma$ -cyclopentadienylide was hydrogenated in ethanol and in glacial acetic acid over Pt-black. Hydrogenation proceeded slowly in ethanol and the hydrogenation rate gradually decreased. In glacial acetic acid there was rapid hydrogenation of the two bonds of the cyclopentadienyl residue and then slow hydrogenation of the pyridine ring.

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# SYNTHESIS OF $\alpha$ -AMINO KETONES

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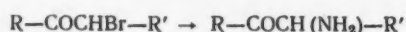
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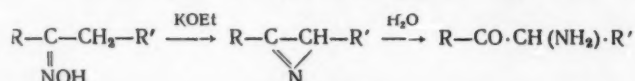
$\alpha$ -Amino ketones have recently attracted interest as raw materials for the synthesis of oxazoles, which are particularly efficient scintillators [1]. In order to prepare new compounds of this class, it became necessary to synthesize  $\alpha$ -amino ketones of various structures. Several methods of synthesizing  $\alpha$ -amino ketones are known and of these, the most important are the amination of  $\omega$ -halo ketones [2]



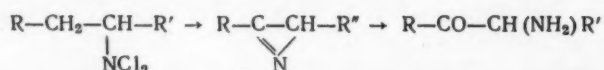
and the reduction of oximino ketones [3]



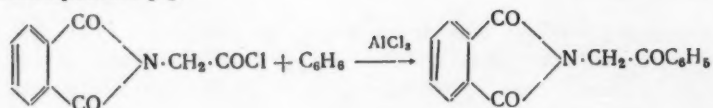
These classical methods, however, have certain drawbacks: The first is the ease with which  $\alpha$ -amino ketones are converted to pyrazines in an alkaline medium and the second is the difficulty of removing tin, which is usually used as the reducing agent.  $\alpha$ -Amino ketones may also be obtained from arylsulfonates of oximes by the Neber rearrangement, which may be used for ketones containing the grouping  $-CH_2-CO-$  [4]:



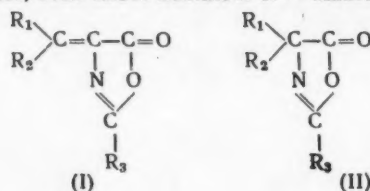
The synthesis of  $\alpha$ -amino ketones from *N,N*-dichloro-*sec*-alkylamines, which was described recently in the literature [5], proceeds by an analogous mechanism:



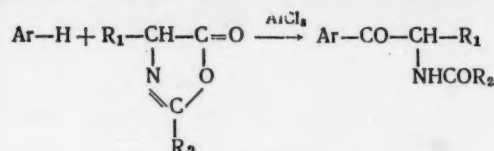
Aromatic  $\alpha$ -amino ketones have also been prepared by condensation of acid chlorides of *N*-acylamino acids with aromatic hydrocarbons in the presence of aluminum chloride. Thus, the acid chloride of *N*-phthalylglycine gives *N*-phthalyl- $\alpha$ -aminoacetophenone [6]:



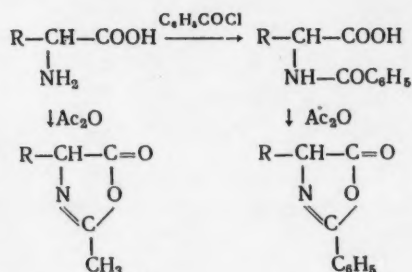
In the present work we present a simpler method of synthesizing aromatic  $\alpha$ -amino ketones, which uses azlactones instead of acid chlorides. Azlactones (derivatives of 5-oxazolone) may be regarded as internal anhydrides of  $\alpha$ -acylamino acids. Azlactones react with a number of substances containing active hydrogen and are of particular interest as intermediates in the synthesis of  $\alpha$ -amino acids,  $\alpha$ -keto acids, and peptides [7]. Of the two types of azlactones, namely, unsaturated (I) and saturated (II), the latter are more reactive and they may be obtained by treatment of  $\alpha$ -acylamino acids or, in many cases, even direct treatment of  $\alpha$ -amino acids with acetic anhydride [8].



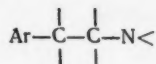
Like anhydrides and acid chlorides, and even more readily than the latter, saturated azlactones condense with aromatic hydrocarbons under the influence of electrophilic catalysts. Using various azlactones under conditions of the Friedel-Crafts reaction, we prepared  $\alpha$ -acylamino ketones according to the following scheme:



The starting amino acids were the lower aliphatic  $\alpha$ -amino acids (glycine, alanine, and  $\alpha$ -aminobutyric acid) and the corresponding aromatic  $\alpha$ -amino acids (phenylglycine and phenylalanine). The azlactones of these amino acids were obtained by treatment of the N-benzoylamino acids with acetic anhydride. In the case of the lower amino acids it was impossible to use direct treatment of the amino acid with acetic anhydride, as it was difficult to separate the excess acetic anhydride from the azlactone formed, because the two compounds boiled at very similar temperatures. In the case of amino acids of higher molecular weight, such as phenylalanine, this method was used satisfactorily.



Benzene was used as the aromatic component in the condensation; the yields obtained exceeded 80% in the case of simple aliphatic  $\alpha$ -amino acid (see the table). In the case of phenylalanine, it was found that together with condensation with benzene according to the scheme presented above, there was also intramolecular cyclization to yield an  $\alpha$ -aminoindanone as in the case of acid chlorides [9]. Only the latter reaction occurred with higher homologs. These results will be reported separately. Experiments were also carried out with toluene and anisole to determine the applicability of the method. The results obtained are given in the table. The  $\alpha$ -acylamino ketones obtained contained the skeleton of  $\beta$ -phenylethylamine

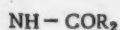


which is present in all substances with a sympathomimetic acid such as adrenaline and ephedrine. The present method makes it possible to synthesize analogs in this series which may have interesting physiological properties. Experiments in this direction are being carried out at the present time. On the other hand,  $\alpha$ -amino ketones are valuable intermediates for the synthesis of such heterocyclic systems as pyrrole, imidazole, and oxazole derivatives. Work is continuing with higher aromatic hydrocarbons in order to prepare  $\alpha$ -acylamino ketones with various aryl radicals, which are difficult to prepare by other methods and are of interest due to the ease of their conversion to disubstituted oxazoles.

#### EXPERIMENTAL

The azlactones used were prepared by methods described in the literature [8]. The preparation method is given only for the azlactones which have not been described previously. A 0.1-mole sample of the azlactone was dissolved in a fivefold amount of benzene and added dropwise with stirring to a suspension of 0.25 mole of anhydrous aluminum chloride in the same amount of benzene. The reaction vessel was fitted with a mechanical stirrer, dropping funnel, and reflux condenser. The azlactone solution was added over a period of 10-20 min; the reaction was weakly exothermic. After the addition, the mixture was heated on a water bath at 50-60° for an hour and then left overnight.

The complex was decomposed with iced water containing a small amount of hydrochloric acid; the benzene layer was separated and dried over sodium sulfate. Removal of the benzene yielded a crystalline product which was purified by recrystallization from ethanol when necessary.



|

$\alpha$ -Acylamino Ketones Ar - CO - CH - R<sub>1</sub>

| Starting materials |  | Ar  | R <sub>1</sub>                                | R <sub>2</sub>                | M.p., °C | Yield, % | Literature |
|--------------------|--|---|---|-------------------------------|----------|----------|------------|
| aromatic component | amino acid                             |   |   |                               |          |          |            |
| Benzene            | Hippuric acid                          | C <sub>6</sub> H <sub>5</sub>                     | H   | C <sub>6</sub> H <sub>5</sub> | 123      | 81       | [11]       |
|                    | N-benzoylalanine                       | C <sub>6</sub> H <sub>5</sub>                     | CH <sub>3</sub>                               | C <sub>6</sub> H <sub>5</sub> | 103      | 82       | [13]       |
|                    | N-benzoyl- $\alpha$ -aminobutyric acid | C <sub>6</sub> H <sub>5</sub>                     | CH <sub>3</sub> CH <sub>2</sub>               | C <sub>6</sub> H <sub>5</sub> | 101      | 84       | [14]       |
|                    | N-acetylphenylglycine                  | C <sub>6</sub> H <sub>5</sub>                     | C <sub>6</sub> H <sub>5</sub>                 | CH <sub>3</sub>               | 134      | 60       | [15]       |
|                    | N-benzoylphenylalanine                 | C <sub>6</sub> H <sub>5</sub>                     | C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> | C <sub>6</sub> H <sub>5</sub> | 144      | 28       |            |
| Anisole            | Hippuric acid                          | { CH <sub>3</sub> O-C <sub>6</sub> H <sub>4</sub> | H   | C <sub>6</sub> H <sub>5</sub> | 113      | 16       |            |
|                    |  | { HO-C <sub>6</sub> H <sub>4</sub>                | H   | C <sub>6</sub> H <sub>5</sub> | 156      | 20       |            |
| Toluene            | N-benzoylalanine                       | CH <sub>3</sub> -C <sub>6</sub> H <sub>4</sub>    | CH <sub>3</sub>                               | C <sub>6</sub> H <sub>5</sub> | 113      | 81       | [16]       |

N-Benzoylaminoacetophenone. The azlactone of hippuric acid (m. p. 86°) was obtained by the method described in the literature [10]. The product from condensation with benzene was identical with N-benzoylaminoacetophenone described in the literature [11].

N-Benzoylamino- $\alpha$ -aminopropiophenone. The azlactone of benzoylalanine (m. p. 39°) was obtained by a known method [10]; condensation with benzene yielded the corresponding derivative of propiophenone, which has been synthesized by a different method [13].

N-Benzoyl- $\alpha$ -aminobutyrophenone. N-Benzoylaminobutyric acid was heated for 15 min on a water bath with a fivefold amount of acetic anhydride and the excess of the latter removed in vacuum to give the azlactone with m. p. 52° (85% yield). A similar condensation with benzene yielded N-benzoylaminobutyrophenone with m. p. 101° (from ethanol). Found: C 76.23; H 6.55; N 5.29%. C<sub>17</sub>H<sub>17</sub>O<sub>2</sub>N. Calculated: C 76.38; H 6.41; N 5.24%. Hydrolysis with a mixture of hydrochloric and acetic acids (1:1) yielded the hydrochloride of  $\alpha$ -aminobutyrophenone with m. p. 178°, which was identical with that described in the literature [14].

N-Acetylidesylamine.  $\alpha$ -Aminophenylacetic acid was heated with 5 parts of acetic anhydride on a water bath (until it dissolved, about an hour) and the excess anhydride was removed in vacuum to give a vitreous azlactone, which was then condensed with benzene. The N-acetylidesylamine obtained melted at 134° (from ethanol). Found: C 75.63; H 6.09; N 5.49%. C<sub>16</sub>H<sub>15</sub>O<sub>2</sub>N. Calculated: C 75.85; H 5.97; N 5.53%.

The 2,4-dinitrophenylhydrazone had m. p. 211° (from ethanol). Found: N 16.14%. C<sub>22</sub>H<sub>19</sub>O<sub>5</sub>N<sub>5</sub>. Calculated: N 16.16%.

Hydrolysis with a mixture of hydrochloric and acetic acids yielded desylamine hydrochloride with m. p. 236°, as compared with 232-235°, which was reported in the literature [15].

$\alpha$ -Benzoylamino- $\beta$ -phenylpropiophenone. From the azlactone of benzoylphenylalanine [2] we obtained  $\alpha$ -benzoyl- $\beta$ -phenylpropiophenone (28%) together with  $\alpha$ -benzoylaminoindanone (33%), which was formed as a result of intramolecular cyclization. The latter will be described elsewhere. The benzoylamino- $\beta$ -phenylpropiophenone melted at 144° (from ethanol). Found: C 80.10; H 5.90; N 4.32%. C<sub>22</sub>H<sub>19</sub>O<sub>2</sub>N. Calculated: C 80.20; H 5.97; N 4.20%.

The 2,4-dinitrophenylhydrazone had m. p. 186° (from acetic acid).

p-Methoxy- $\omega$ -benzoylaminoacetophenone. The azlactone of hippuric acid was condensed with anisole (1 mole: 2 moles) by the addition of aluminum chloride to a solution of the two reagents. The reaction was strongly exothermal; the reaction mixture was heated at 70-75° for an hour. After decomposition of the complex with very

dilute acid, the reaction mixture was extracted with ether and the ether layer washed with 5% sodium hydroxide solution. From the ether layer we obtained the ketone given in the title with m. p. 113°, which has been synthesized by a different method [16]. The alkaline extract was acidified and extracted to give approximately the same amount of p-hydroxybenzoylaminoacetophenone which was formed as a result of hydrolysis of the ester group. The total yield was 36%. The p-hydroxy-N-benzoylaminoacetophenone had m. p. 156° (from ethanol). Found: C 70.34; H 5.02; N 5.36%.  $C_{15}H_{13}O_3N$ . Calculated: C 70.58; H 5.13; N 5.49%.

The 2,4-dinitrophenylhydrazone had m. p. 218° (from acetic acid). Found: N 16.02%.  $C_{21}H_{17}O_6N_5$ . Calculated: N 16.09%.

p-Methyl- $\alpha$ -benzoylamino propiophenone. The azlactone of benzoylalanine (see experiment 2) and toluene yielded an amino ketone with m. p. 114° (from ethanol). It was not established whether the product obtained was an individual substance or a mixture of ortho- and para-isomers. Found: C 76.57; H 6.36; N 5.38%.  $C_{17}H_{17}O_2N$ . Calculated: C 76.38; H 6.41; N 5.24%.

#### SUMMARY

A new method is described for synthesizing aromatic  $\alpha$ -amino ketones with the general formula  $Ar-CO-CH-R_1$ , which is based on the condensation of azlactones with benzene in the presence of aluminum chloride.

NHCOR<sub>2</sub>

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# SYNTHESIS OF CYCLIC $\alpha$ -AMINO KETONES

E. Chiorănescu and L. Bukhen-Byrlădryanu

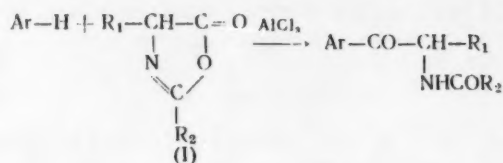
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Translated from *Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk*,

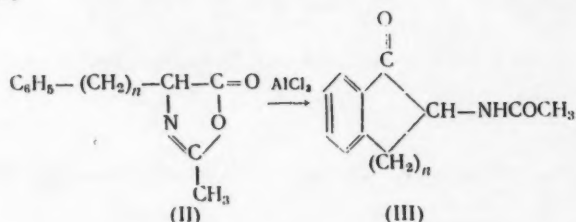
No. 1, pp. 149-151, January, 1961

Original article submitted June 4, 1960

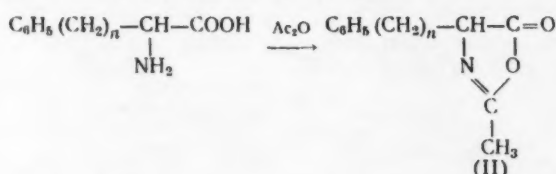
In a previous communication [1] we showed that saturated azlactones (I) react with aromatic compounds in the presence of aluminum chloride, behaving like acid anhydrides. This yields  $\alpha$ -acylamino ketones according to the scheme:



In this investigation it was observed that like acid chlorides [2], azlactones of the type (II) ( $n = 1, 2$ , and 3) give cyclic  $\alpha$ -acetyl amino ketones (III) when treated with aluminum chloride in carbon disulfide, as a result of an intramolecular condensation.



Azlactones of this type are prepared smoothly by treatment of appropriate  $\alpha$ -amino acids with acetic anhydride [3]:



By this method we synthesized: 2-acetylaminoindanone, which is usually obtained from indanone through 2-nitrosoindanone with subsequent reduction with stannic chloride [4]; 2-acetylaminotetralone-1, which was first obtained by Neber by rearrangement of tetralone oxime arylsulfonate [5], and was recently obtained from 1,2,3,4-tetrahydro-1-naphthylamine by conversion to the dichloramine with subsequent treatment with sodium methylate [6]; 4-acetylaminobenzosuberone, whose synthesis has not been given in the literature. Hydrolysis yielded the hydrochlorides of these  $\alpha$ -amino ketones. In view of the ease with which the azlactones of this series are obtained, this method is a simple route to the synthesis of cyclic  $\alpha$ -amino ketones.

## EXPERIMENTAL

The azlactones were obtained by heating appropriate amino acids with five parts of acetic anhydride on a water bath for 10-15 min. The excess acetic anhydride was removed at as low a pressure as possible (1-2 mm Hg) and with gentle heating on a water bath (35-40°). A 0.1 mole portion of the azlactone was dissolved in a five- or

tenfold amount of carbon disulfide. Into a flask fitted with a mechanical stirrer were placed 0.3 mole of anhydrous aluminum chloride and approximately 5 parts of carbon disulfide, and the azlactone solution was added dropwise at room temperature. The reaction was weakly exothermal. The reaction mixture was boiled on a water bath for an hour and left at room temperature overnight. After decomposition of the complex with iced water, the carbon disulfide was separated and the aqueous layer extracted continuously with ether. Removal of the ether yielded the crystalline  $\alpha$ -acetyl amino ketone, which was recrystallized from water. The yield was approximately 65%.

2-Acetylaminoindanone (III, n = 1) had m. p. 155-156°. It was prepared from 2-methyl-4-benzyl-5-oxazolone (II, n = 1), which, in its turn, was synthesized from  $\alpha$ -phenylalanine and acetic anhydride [7]. Found: C 69.76; H 6.12; N 7.42%.  $C_{11}H_{11}O_2N$ . Calculated: C 69.80; H 5.80; N 7.41%.

The 2,4-dinitrophenylhydrazone had m. p. 254° (from acetic acid). Found: N 18.80%.  $C_{17}H_{15}O_5N_5$ . Calculated: N 18.96%.

Hydrolysis with dilute hydrochloric acid (1:1) yielded  $\alpha$ -aminoindanone hydrochloride with m. p. 237-238° (with decomposition), which was identical with that described in the literature [4]. In the same way we obtained benzoylaminoindanone from N-benzoyl- $\alpha$ -phenylalanine through the azlactone; it had m. p. 190°. Found: C 76.32; H 5.24; N 5.58%.  $C_{16}H_{13}O_2N$ . Calculated: C 76.49; H 5.17; N 5.57%.

2-Acetylaminotetralone-1 (III, n = 2) had m. p. 127-128° and was synthesized from 2-methyl-4-phenylethyl-5-oxazolone [b. p. 138-139° (2 mm)], which was prepared from  $\gamma$ -phenyl- $\alpha$ -acetylaminobutyric acid and acetic anhydride [8]. The yield of the cyclization was 63%. Found: C 71.11; H 6.62; N 6.85%.  $C_{12}H_{13}O_2N$ . Calculated: C 70.91; H 6.45; N 6.89%.

The 2,4-dinitrophenylhydrazone had m. p. 256° (from acetic acid). Found: N 18.34%.  $C_{18}H_{17}O_5N_5$ . Calculated: N 18.27%. The hydrochloride, which was obtained as a result of hydrolysis with hydrochloric acid, crystallized with one molecule of water and melted at 203-204°, in contrast to the anhydrous product of Neber, which melted at 117°. This has recently been pointed out by other authors [16].

4-Acetylaminobenzosuberone-3 (III, n = 3).  $\delta$ -Phenyl- $\alpha$ -aminovaleric acid was obtained by condensation of cinnamaldehyde with acetylglycine [9], and then reduced with sodium amalgam to butene-4-phenyl-1-acetyl amino-1-carboxylic acid (m. p. 116°). Catalytic hydrogenation of the latter in alcohol in the presence of platinized charcoal (5%), removal of the solvent in vacuum, and recrystallization from water gave an acetyl amino acid with m. p. 149-150° in a yield of 70%, calculated on cinnamaldehyde. Found: C 66.36; H 7.28%.  $C_{13}H_{17}O_3N$ . Calculated: C 66.43; H 7.51%. The azlactone was obtained by the method given and recrystallized after removal of the excess acetic anhydride; it had m. p. 59-60° and the yield was 92-93%. Treatment with aluminum chloride in carbon disulfide gave the acetyl amino ketone (III) with m. p. 137° in 64% yield. Found: C 71.57; H 6.94; N 6.50%.  $C_{13}H_{15}O_2N$ . Calculated: C 71.86; H 6.96; N 6.40%. The 2,4-dinitrophenylhydrazone had m. p. 237° (from ethanol). Found: N 17.64%.  $C_{19}H_{19}O_5N_5$ . Calculated: N 17.81%.

#### SUMMARY

A simple method is described for synthesizing cyclic  $\alpha$ -amino ketones by intramolecular cyclization of azlactones under the action of aluminum chloride.

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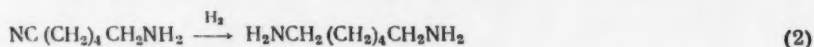
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SELECTIVE REDUCTION OF ADIPONITRILE TO  
 $\epsilon$ -AMINOCAPRONITRILE ON A NICKEL  
BORIDE CATALYST

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An investigation of the selectivity of catalysts in the hydrogenation of adiponitrile is of interest in two respects for determining the steps of the process



and as a method of preparing the nitrile of an amino acid, which is readily converted to an  $\epsilon$ -amino acid by hydrolysis. A brief review of literature data on this problem is given in [1].

As was shown previously, in hydrogenation under pressure on a highly active skeletal nickel catalyst, it is difficult to stop the process at the formation of the aminonitrile (1). The selective hydrogenation of the dinitrile to the aminonitrile was found to be possible in the presence of partly deactivated skeletal nickel catalysts if the reaction was stopped after the absorption of 2 mol.-equiv. of hydrogen [1]. The process proceeds specifically on the nickel boride catalyst used in the present work, in contrast to skeletal nickel. The aminonitrile formed is not hydrogenated under certain conditions, but not all the dinitrile taken for the reaction can be converted to aminonitrile. It was found that this is explained by adsorption displacement of the dinitrile by the aminonitrile accumulating in the reaction mixture. On the other hand, the aminonitrile is not displaced from the catalyst by hexamethylenediamine. The latter indicates that the greater difficulty in effecting stage (2) is caused by the different reactivities of the CN groups in the dinitrile and aminonitrile molecules.

Considerably less secondary amine was formed in experiments on partial hydrogenation of the dinitrile than in its complete hydrogenation. In accordance with this, the yield of secondary amines was the same whether dinitrile or aminonitrile was used for the reaction. Thus, secondary amines are formed in stage 2. When the reaction was carried out in the absence of ammonia, the yield of secondary amines increased still further. These results confirm the aldimine mechanism for the formation of secondary amines [2].

#### EXPERIMENTAL

The hydrogenation was carried out in a 0.5 liter steel autoclave, which was charged with 50 ml (0.455 mole) of the dinitrile and the required amount of catalyst and ammonia. Hydrogen was introduced to an initial pressure of 100 atm, heating was begun, and when the given temperature was reached, the autoclave was rotated. The reaction products were separated from the catalyst and distilled to give fractions with the following boiling points: I - 137° (hexamethylenimine), the boiling point of the azeotrope with water is 95°; II - 95-100° (20 mm) (hexamethylenediamine); III - 118-120° (20 mm) ( $\epsilon$ -aminocapronitrile). The high-boiling residue consisted mainly of unreacted dinitrile with some bis-hexamethylenetriamine (triamine). The amine content of all the fractions was determined acidimetrically. The refractive index of the aminonitrile fraction was also determined. The catalysts were prepared by exhaustive extraction of powdered Ni-Ti-Al alloys with 10% aqueous sodium hydroxide solution for 2 hr at 95°; after being washed with water until neutral to phenolphthalein they were stored under alcohol at 1-5°.

The nickel boride catalyst was obtained by the following procedure [3]. With stirring, 60 ml of a 20% aqueous solution of sodium borohydride was gradually added to a mixture of 250 ml of a 10% aqueous solution of nickel

chloride (or acetate) and 10 ml of a 10-30% solution of chromium nitrate (or sulfate) at such a rate that the temperature of the reaction mixture did not exceed 50°. The dark precipitate obtained was transferred to a funnel with a porous glass filter, washed until neutral to phenolphthalein, and stored under alcohol at 1-5°. The compositions of the alloys used, the experimental conditions, and the results of analyzing the reaction mixture are given in the tables.

TABLE 1. Experimental Conditions: Hydrogen Pressure 100 atm, Molar Ratio of Dinitrile: Ammonia, 1:2, Catalyst 10 g

| Expt. No. | Composition of alloy, wt. % | Experimental conditions |           | Composition of reaction products in fractions, wt. % |    |     |                   |            |
|-----------|-----------------------------|-------------------------|-----------|--|----|-----|-------------------|------------|
|           |                             | temp., °C               | time, min | I  | II | III | residue tri-amine | di-nitrile |
| 1         | Ni-Al 50-50                 | 80                      | 25        | 5  | 27 | 53  | 3                 | 12         |
| 2         | Ni-Al-Ti 48-48-4            | 80                      | 20        | 4  | 22 | 53  | 6                 | 15         |
| 3         | The same 46-47-7            | 80                      | 40        | 3  | 17 | 57  | 4                 | 19         |
| 4         | " 30-50-20                  | 80                      | 55        | 4  | 13 | 51  | 4                 | 28         |
| 5         | " 30-50-20                  | 60                      | 210       | 4  | 14 | 51  | 4                 | 27         |

TABLE 2. Experimental Conditions: Molar ratio of Dinitrile: Ammonia 1:2-1:3

| Expt. No. | Nickel boride catalyst  | Experimental conditions |                                |                       |                 | Composition of reaction products in fractions, wt. % |    |     |                   |            |
|-----------|-------------------------|-------------------------|--------------------------------|-----------------------|-----------------|--|----|-----|-------------------|------------|
|           |                         | temp. °C                | initial hydrogen pressure, atm | amount of catalyst, g | expt., time, hr | I  | II | III | residue tri-amine | di-nitrile |
| 6         | Unmodified              |                         |                                |                       |                 |  |    |     |                   |            |
| 7         | The same                | 50                      | 100                            | 10                    | 2,5             | 6  | 14 | 49  | 4                 | 27         |
| 8         | Modified                | 80                      | 100                            | 10                    | 2,5             | 6  | 16 | 52  | 4                 | 23         |
| 9         | "                       | 75                      | 95                             | 10                    | 6               | 4  | 2  | 45  | 4                 | 45         |
| 10        | "                       | 80                      | 100                            | 10                    | 4               | 3  | 3  | 61  | 3                 | 30         |
| 11        | "                       | 90                      | 95                             | 10                    | 4,5             | 5  | 17 | 54  | 2                 | 22         |
| 12        | "                       | 120                     | 120                            | 10                    | 4               | 13   | 75 | 0   | 10                | 2          |
| 13        | "                       | 80                      | 50                             | 10                    | 2               | 0  | 0  | 10  | —                 | 90         |
| 14        | "                       | 80                      | 75                             | 10                    | 4,5             | 3  | 3  | 40  | 6                 | 48         |
| 15        | "                       | 75                      | 95                             | 20                    | 1,5             | 17   | 74 | 0   | 7                 | 22         |
| 16        | "                       | 80                      | 100                            | 20                    | 0,8             | 5  | 7  | 45  | 3                 | 40         |
| 17        | "                       | 65                      | 100                            | 20                    | 5,5             | 5  | 7  | 49  | 4                 | 35         |
| 18        | Cobalt boride, modified | 110                     | 100                            | 5                     | 4               | 3  | 7  | 52  | 4                 | 34         |
|           |                         | 80                      | 100                            | 20                    | 1,5             | 4  | 17 | 41  | 2                 | 36         |

Hydrogenation over Ni-Ti catalyst. In experiments 1-7, 15, and 18, the reaction was stopped after the absorption of approximately 2 mol.-equiv. of hydrogen (when hydrogenation was half complete). Experiments 1-4, which were carried out at 80° and 100 atm (Table 1), show that the addition of 4% of Ti to the catalyst had little effect on the rate and direction of the reaction. With an increase in the amount of titanium in the catalyst to 7 and 20%, the reaction time increased by a factor of 1.5-2. At the same time the aminonitrile content of the catalyzate hardly changed, while the diamine yield fell from 27 to 17 and 13%, and the amount of unreacted dinitrile increased correspondingly from 12% (experiment 1) to 19% (experiment 3) and 28% (experiment 4). The catalyzate obtained in experiment 5, which was carried out at a lower temperature (60°), did not differ in composition from the catalyzate of experiment 4, but the reaction time increased considerably.

Hydrogenation over nickel boride catalyst. As experiments 6 and 7 show, the activity of the nickel boride catalyst was very much lower than that of the skeletal nickel: The time for half hydrogenation was 6 times greater in the presence of the former (Table 2). The catalyzates from these experiments, which were stopped when approximately 2 mol.-equiv. of hydrogen had been absorbed, were found to contain 49-52% of aminonitrile and 14-16% of diamine. The nickel boride catalyst modified with chromium was found to be even less active: The time for

half hydrogenation increased by a factor of approximately 2. In contrast to the cases of all the catalysts we tested previously, with this catalyst, the fall in pressure stopped after the absorption of approximately 2 mol.-equiv. of hydrogen, i.e., the reaction stopped (experiments 8-14, 16, and 17). Experiments 8 and 9 show that at 75-80° and 100 atm, the reaction mixture with promoted catalyst contained mainly  $\epsilon$ -aminocapronitrile (45 and 61%) and unreacted dinitrile (45 and 30%), and little hexamethylenediamine (3 and 5%) was formed. When the temperature was raised to 90°, the diamine yield increased to 17% (experiment 10). Four moles of hydrogen was absorbed at 120° and the diamine yield was 75%, while aminonitrile was absent from the reaction products. At the same time, 13% of cyclohexamethylenimine and 10% of triamine were formed (experiment 11). The effect of pressure was studied in experiments 12-14. At 50 atm, the reaction stopped after the absorption of 7.5% of the required amount of hydrogen. The catalyzate from this experiment contained 10% of aminonitrile and 90% of unreacted dinitrile, while no diamine or cyclic imine was present. In an experiment at 75 atm, we obtained 40% of aminonitrile and 3% of diamine. When twice the amount of catalyst was used there was complete hydrogenation of the dinitrile with the formation of 74% of diamine and 17% of cyclic imine. In an analogous experiment (15), which was stopped after the absorption of  $\sim 2$  mol.-equiv. of hydrogen, 45% of aminonitrile and only 7% of diamine were formed. Experiment 16, which was carried out at a lower temperature (65°) and with twice the amount of catalyst, yielded 49% of aminonitrile and 7% of diamine. With a decrease in the amount of catalyst to 10% (experiment 17), the reaction began only at 110° and the composition of the half-hydrogenation products was approximately the same as in experiments 8 and 9.

TABLE 3. Experimental Conditions: Initial Hydrogen Pressure 100 atm; Catalyst - Modified Nickel Boride

| Expt. No. | Compound hydrogenated                           | Weight ratio of mixture components | Experimental conditions |                                 |                       |                     | Composition of reaction products, wt. % |    |     |           |            |
|-----------|---|------------------------------------|-------------------------|---------------------------------|-----------------------|---------------------|---|----|-----|-----------|------------|
|           |   |                                    | Temp., °C               | substance taken: ammonia, moles | amount of catalyst, g | experiment time, hr | I                                       | II | III | residue   |            |
|           |   |                                    |                         |                                 |                       |                     |   |    |     | tri-amine | di-nitrile |
| 19        | ε -Aminocapronitrile                            | —                                  | 80                      | 1:2,4                           | 10                    | 2                   | 10% of hydrogen was absorbed            |    |     |           |            |
| 20        | ε -Aminocapronitrile                            | —                                  | 110                     | 1:2,4                           | 10                    | 2                   | 15                                      | 76 | —   | 8         | (1)*       |
| 21        | Adiponitrile: ε -aminocapronitrile              | 5,5:4,5                            | 80                      | 1:2                             | 10                    | 2                   | 2                                       | 5  | 35  | 3         | 55         |
| 22        | »   | 5,3:4,7                            | 80                      | 1:2                             | 10                    | 3                   | 3                                       | 8  | 36  | 3         | 50         |
| 23        | »   | 6:4                                | 80                      | 1:2                             | 20                    | 2                   | 2                                       | 2  | 65  | 3         | 28         |
| 24        | ε -Aminocapronitrile : 1,6-hexamethylenediamine | 1:1                                | 85                      | 1:2                             | 10                    | 1,5                 | 8% of hydrogen was absorbed             |    |     |           |            |
| 25        | »   | 1:1                                | 120                     | 1:2                             | 10                    | 2                   | 14                                      | 76 | 0   | 8         | (2)*       |
| 26        | Adiponitrile : 1,6-hexamethylenediamine         | 1:1                                | 85                      | 1:2                             | 10                    | 2                   | 7                                       | 3  | 25  | 9         | 56         |
| 27        | »   | 1:1                                | 120                     | 1:1,5                           | 10                    | 1,5                 | 17                                      | 50 | 2   | 16        | 15         |
| 28        | Adiponitrile                                    | —                                  | 80                      | No NH <sub>3</sub>              | 10                    | 7                   | 9                                       | 42 | 29  | 5         | 15         |
| 29        | »   | —                                  | 120                     | No NH <sub>3</sub>              | 10                    | 5                   | 20                                      | 64 | —   | 11        | (5)*       |

\* Untitratable part, which probably consisted of high-molecular polyamines.

The results of experiments with modified nickel boride catalyst show very clearly that the second nitrile group of the dinitrile is hydrogenated with much more difficulty than the first; namely, at a higher temperature (110-120°) or with a larger amount of catalyst (40 weight %). Under conditions similar to experiment 15 with a cobalt boride promoted catalyst, 41% of aminonitrile and 36% of unreacted dinitrile were obtained. Thus, hydrogenation of adiponitrile proceeds in steps on a cobalt boride catalyst (experiment 18).

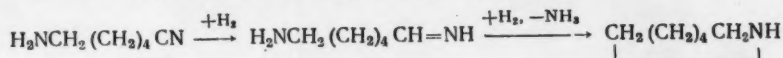
The data obtained led us to the conclusion that under the optimal conditions (in the presence of ammonia, 20% of catalyst, temperature 75-80°, initial hydrogen pressure 95-100 atm), the  $\epsilon$ -aminocapronitrile formed in the reaction is not hydrogenated on a nickel boride catalyst. We confirmed this hypothesis with a special experiment, in which it was established that the aminonitrile was not reduced under these conditions:  $\sim 10\%$  of the hydrogen required

for half hydrogenation was absorbed (experiment 19). When the temperature was raised to 110°, there was further absorption of hydrogen and 76% of hexamethylenediamine was formed (experiment 20) (Table 3).

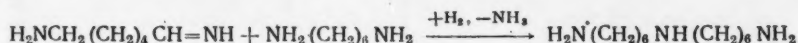
**Effect of reaction products.** In experiments on this catalyst (20 wt. %) at 80°, the absorption of hydrogen ceased when the reaction mixture still contained a considerable amount of unreacted dinitrile. It was important to establish what interferes with the hydrogenation of the first nitrile group of all the dinitrile molecules taken for the reaction. It may be considered that at the beginning of the process, when the dinitrile concentration in the catalyzate is high, the formation of aminonitrile does not affect the reaction rate. As the aminonitrile concentration in the reaction mixture increases, the adsorption displacement of the dinitrile by it begins and the hydrogen absorption rate falls. When the aminonitrile concentration becomes considerable (~50%), hydrogenation of the dinitrile ceases completely.

To check this hypothesis, we carried out experiments on the hydrogenation of the dinitrile mixed with the aminonitrile under conditions where the aminonitrile was hardly hydrogenated (80°, 100 atm, and 20 wt. % of catalyst). The results obtained showed that practically the whole of the dinitrile taken remained unchanged and only a small part of the aminonitrile was converted to the diamine and secondary amines (experiments 21 and 22). Even when the amount of catalyst was doubled (experiment 23), only part of the dinitrile mixed with aminonitrile was hydrogenated. The hydrogen absorption rate in the hydrogenation of the dinitrile alone in experiment 11 was 4 times greater than in its hydrogenation in a mixture with aminonitrile (experiment 21). In the first case, 20 liters of hydrogen was absorbed in an hour and in the second case, only 5 liters. The results of these experiments confirm the hypothesis that there is adsorption displacement of the dinitrile by the aminonitrile. On the other hand, the aminonitrile (stage 2) is not displaced by the diamine: In the hydrogenation of the aminonitrile mixed with the diamine (experiment 25), the same yields of diamine and cyclohexamethyleneimine were obtained as in its reduction in the absence of diamine (experiment 11). Experiment 26 shows that 45% of the dinitrile was converted at 85° in a mixture with hexamethylenediamine, while the dinitrile was hardly reduced at all in a mixture with aminonitrile under analogous conditions (experiments 21 and 22).

**Mechanism of secondary amine formation.** As has been reported above, secondary amines (imine and triamine) are formed together with hexamethylenediamine in the hydrogenation of the dinitrile. In accordance with the aldime mechanism of the reaction, the imine can only be formed in stage 2:



and should not be formed in stage 1 of the hydrogenation of the dinitrile. In actual fact, in all our experiments the imine was formed largely during complete hydrogenation of the dinitrile (13-14% yield) and in an insignificant amount (2.5%) during half-hydrogenation. The imine yield was the same whether the aminonitrile (experiment 20) or dinitrile (experiment 11) was used for the reaction. These facts indicate that the imine is formed during the hydrogenation of the aminonitrile [4]. In contrast to the imine, which is formed by an intramolecular reaction of the imino and amino groups, the triamine is formed by an intermolecular process:



An increase in the concentration of compounds containing an amino group in the reaction mixture should therefore lead to an increase in the yield of triamine. In actual fact, during the reduction of the dinitrile in a mixture with the triamine, much more triamine than usual was formed both during half-hydrogenation (experiment 26) and during complete hydrogenation (experiment 27).

## SUMMARY

1. The hydrogenation of adiponitrile to  $\epsilon$ -aminocapronitrile on a nickel boride catalyst and on skeletal nickel with titanium added was investigated. With an increase in the amount of titanium in the skeletal nickel catalyst, the selectivity of the latter increased.
2. The dinitrile was hydrogenated selectively to the aminonitrile on the nickel boride catalyst: 50-60% of the aminonitrile and only 2-5% of the diamine were formed under the optimal conditions.
3. The reason for the incomplete conversion of the dinitrile to the aminonitrile under half-hydrogenation conditions is adsorption displacement of the dinitrile by the aminonitrile.

4. In the hydrogenation of the dinitrile, cyclohexamethyleneimine is formed during the second stage of the process, while the formation of bishexamethylenetriamine increases appreciably when the dinitrile is hydrogenated in a mixture with hexamethylenediamine. As with other catalysts, ammonia suppresses the formation of both secondary amines. These facts confirm the aldimine mechanism for the hydrogenation of the dinitrile.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

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## BRIEF COMMUNICATIONS

### THE DETONATION PARAMETERS OF TG 68/32

#### HETEROGENEOUS CHARGES

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In the present work the parameters for the detonation wave front of heterogeneous charges of trotyl-hexogene TG 68/32 (68% by weight of trotyl and 32% hexogene) with a density of  $1.672 \text{ g/cm}^3$ , have been measured. The charges were prepared by melting trotyl and adding pieces of high density hexogene (density approximately  $1.80 \text{ g/cm}^3$ ) of a different size. The diameter of the charges used equalled 60 mm, the length together with the lens type detonator, 100 mm.

The method [1] is based on the calculation of the parameters of the descending detonating wave front from known values of the parameters of the shock wave in a metal tightly pressed to the face end of the charge being investigated. In this investigation, aluminum was used as the metal. The parameters of the shock wave in the metal were determined by measuring the free surface velocity imparted to thin metal plates. For all charges investigated the free surface velocity decreases linearly with increase in the thickness of the metal plate (from 3 up to 20 mm). Calculation of the detonation wave parameters was carried out from the values of the parameters of the shock wave in the metal at a depth of 1 mm.

| No. of test | Dimension of hexogene $l$ , mm | $D$ , km/sec | $P \cdot 10^9$ , bar |
|-------------|--------------------------------|--------------|----------------------|
| 1           | $10 < l < 14$                  | 8,32         | 239                  |
| 2           | $5 < l < 10$                   | 8,25         | 245                  |
| 3           | $\sim 0,05$                    | 7,56         | 255                  |

The experimental results obtained are reproduced in the table. The pressure  $P$  at the detonation wave front was determined with a precision of approximately 2-3%. The detonation velocity  $D$  was determined by the ionization method on bases of approximately 60 mm which ensured a precision of about 1% for heterogeneous charges and about 0.2-0.3% for homogeneous charges.

As can be seen from the table the detonation velocities of coarse size hexogene charges (heterogeneous charges 1 and 2) are significantly higher than the detonation velocity of homogeneous charges (3), while the pressure at the wave front decreases compared with the pressure in homogeneous charges. This may be explained by the fact that the detonation velocity in these charges is determined by its propagation from the pieces of hexogene. Figure 1 presents the photograph of the face end of a charge of TG 68/32 with pieces of hexogene with the dimension  $10 < l < 14 \text{ mm}$ , and the photograph of the initiation of the detonation wave at this face end is obtained by means of a high speed recording camera. It is very clear from the photograph that the wave front first appears at the hexogene pieces. The white parts on the photograph of the face end of the charge correspond to hexogene, the dark to trotyl. Obviously the detonation velocity measured for charges containing coarse lumps of hexogene is more than the thermodynamically possible total energy for the high explosive,  $Q_{TG}$ .

The detonation velocity propagated from the hexogene pieces is determined by the energy which is evolved by the explosion of hexogene  $Q_G$ , which is more than  $Q_{TG}$ . As a consequence of this fact, the detonation velocity of the heterogeneous charges is more than the detonation velocity of the homogeneous charges. The pressure-specific volume ( $P$ - $V$ ) curve is reproduced in Fig. 2. In this figure the curve OA2 is the shock adiabat of the explosive, the curve C1D is the shock adiabat of the products of the explosive, corresponding to the total overall energy of the high explosive. The straight lines from point 0 are Michelson lines corresponding to the different detonation velocities. The higher the detonation velocity the greater the slope of these lines.

As has been established by the present day hydrodynamic theory of detonation (first proposed by Zeldovich [2]), point 1 (Jouget point), the tangency point of Michelson's line with the adiabat of the explosive products C1D,

corresponds to normal detonation (number 3, table) for this adiabat. Points of the adiabat C1D lying above point 1 (highly compressed region of detonation) are not realized in stationary detonation because the sonic velocity with respect to the material behind the wave front corresponding to these points is more than the velocity of propagation of the wave front. The points of the adiabat C1D lower than point 1 (insufficiently compressed region of detonation up to the point D) are not obtained by the shock mechanism of the detonation for another reason. The high explosive must in this case be compressed by the shock mechanism up to the pressures above point 2, e.g., up to point 5. Behind the shock wave front the variation in the composition of the material in the coordinates (P-V) follows the Michelson line 045.

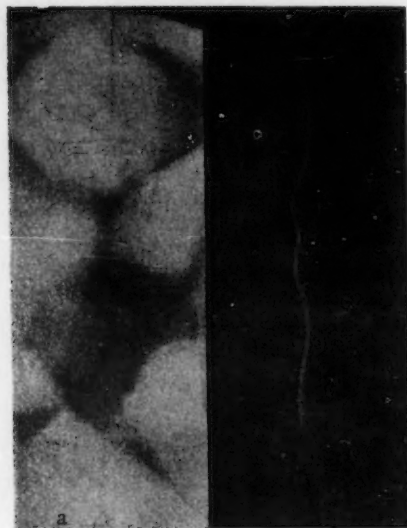


Fig. 1. (a) Photograph of face end of charge; (b) initiation of detonation at this face. Dimension of hexogene pieces in this charge  $10 < l < 14$  mm.

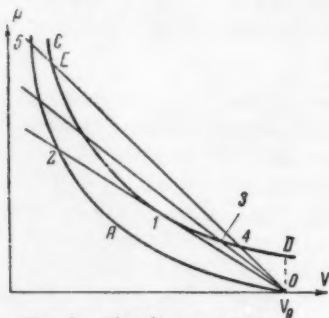


Fig. 2. The diagram P-V.

Point E corresponds to the total evolution of energy, and therefore a further change in composition along the straight line is not possible. Consequently the transition from point E to point 4 must develop intermittently, but as proved by theory, rarefaction shock waves do not exist. A low compressed regime of detonation may be produced if the velocity of the process is determined not by the shock wave but, e.g., as suggested by Zel'dovich and Kompaneets [3], by exciting sparks to follow each other at a definite velocity along the charge, producing the reaction. The independent propagation of detonation along the separate pieces of hexogene in our case play the part of spark gaps. In the case of an insufficiently compressed region of detonation the wave front must spread because the reaction is excited in different centers. Obviously the parameters measured in the present work correspond to that point of the wave where the reaction is completely finished.

Thus it is possible to arrive at the conclusion, in our opinion, that due to the development of insufficiently compressed conditions of detonation in heterogeneous charges the pressure at the wave front is lower than the pressure attained in homogeneous charges. It should be noted that if the shock adiabat of the products of the explosive C1D is known, then the experimental results obtained may be calculated theoretically on the basis of information on the detonation velocity only.

#### SUMMARY

1. In this work the parameters for the detonation wave front in cast explosives, density  $1.672 \text{ g/cm}^3$ , containing 68% trotyl with the addition of 32% of very dense particles of hexogene of different dimension, have been measured.

2. With an increase in the particle dimensions the detonation velocity of the charges investigated increases, but the pressure at the wave front falls in comparison with the corresponding parameters in charges containing finely dispersed hexogene.

3. The explanation of this phenomenon lies in the fact that in heterogeneous charges an insufficiently compressed region of detonation occurs.

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# SYNTHESIS OF $\omega$ -AMINODODECANOIC ACID

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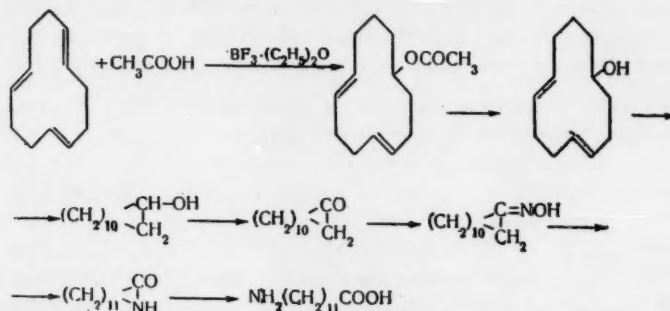
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In the series of the  $\omega$ -aminocarboxylic acids  $\text{NH}_2(\text{CH}_2)_n\text{COOH}$ ,  $\omega$ -aminododecanoic acid  $\text{NH}_2(\text{CH}_2)_{11}\text{COOH}$  had not been prepared hitherto. We synthesized  $\omega$ -aminododecanoic acid starting from the accessible *trans, trans*, *trans*-cyclododecatriene-1,5,9 [1]. The synthesis was carried out according to the following scheme:



On being heated at 100° with acetic acid in the presence of the ethyl ether adduct of boron trifluoride, *trans, trans, trans*-cyclododecatriene added one molecule of acetic acid with the formation of *trans, trans*-1-acetoxycyclododecadiene-5,9, which after saponification with alcoholic caustic yielded the corresponding alcohol. The latter could be easily hydrogenated to cyclododecanol, which was oxidized to cyclododecanone with chromic acid anhydride. Cyclododecanone oxime was converted into  $\omega$ -dodecalactam by rearrangement under the action of sulfuric acid.  $\omega$ -Dodecalactam proved to be resistant to hydrolysis with acids: It remained unchanged after being boiled for many hours in a concentrated hydrochloric or hydrobromic acid solution. Hydrolysis could be easily carried out by heating the  $\omega$ -dodecalactam with aqueous-alcoholic caustic at 150-160°. The free amino acid separated on acidification with dilute hydrochloric acid of the aqueous solution of the potassium salt.

## EXPERIMENTAL

**Trans,trans-1-acetoxycyclododecadiene-5,9.** A solution of 50 g of *trans,trans,trans*-cyclododecatriene-1,5,9 in 200 ml of glacial acetic acid was heated for 30 hr at 100° in the presence of 2.5 g of the ether adduct of boron trifluoride. After the acetic acid had been distilled off in vacuum, the residue was diluted with water and extracted with ether. The ethereal solution was washed with a solution of sodium carbonate and dried with sodium sulfate. The ether was distilled off and the residue distilled in vacuum. Besides 28.5 g of the initial triene, 20 g of *trans,trans*-1-acetoxycyclododecadiene were obtained; b. p. 110-113° (2.5 mm);  $n_D^{20}$  1.4877;  $d_4^{20}$  0.9902; found MR 64.56; calculated MR 65.23. Found: C 75.39, 75.44; H 9.91, 9.98%.  $\text{C}_{14}\text{H}_{22}\text{O}_2$ . Calculated: C 75.67; H 9.91%.

**Trans,trans-1-hydroxycyclododecadiene-5,9.** A solution of 12.5 g of acetoxycyclododecadiene and 5.7 g of potassium hydroxide in 60 ml of ethyl alcohol was boiled for 7 hr. After the reaction mixture had been diluted with water, the oily layer which separated was extracted with ether and the ether solution dried with sodium sulfate. The ether was distilled off and the residue distilled in vacuum. The yield amounted to 8 g of *trans,trans*-hydroxycyclododecadiene with a b. p. of 125-127° (8 mm); m. p. 66.5-67° (from petroleum ether). Found: C 80.11, 79.88; H 11.21, 11.35%.  $\text{C}_{12}\text{H}_{20}\text{O}$ . Calculated: C 79.98; H 11.12%.

**Cyclododecanol.** Six g of *trans,trans*-hydroxycyclododecadiene in 25 ml of ethyl alcohol were reduced in the presence of Raney nickel at atmospheric pressure. The catalyst was filtered off. The filtrate was diluted with water and

extracted with benzene. After removal of the solvent the solid residue was recrystallized from petroleum ether, whereupon 5.8 g of cyclododecanol with a m. p. of 78-79° was obtained. Data published in the literature [2]: m. p. 80°.

Cyclododecanone. To a solution of 3 g of chromic acid anhydride in 30 ml of acetic acid and 2 ml of water, a solution of 5.4 g of cyclododecanol in 20 ml of acetic acid was added. The mixture was allowed to stand for 12 hr at room temperature, after which it was diluted with water and extracted with ether. The ethereal solution was washed with a solution of sodium carbonate and dried with sodium sulfate. After elimination of the solvent the residue was recrystallized from ethyl alcohol. The yield of cyclododecanone was 4.5 g and its m. p. 58-59°. Published data [3]: m. p. 59°.

Cyclododecanone oxime. A mixture of 4.5 g of cyclododecanone, 3 g of hydroxylamine hydrochloride, and 3 g of sodium bicarbonate in 40 ml of methyl alcohol was heated for 2 hr under boiling and then poured into water. The solid precipitate was filtered off. On recrystallization from methanol, 4 g of cyclododecanone oxime with a m. p. of 133-134° was obtained. Published data [4]: m. p. 132°.

$\omega$ -Dodecalactam. A solution of 4 g of cyclododecanone oxime in 3 ml of 91% sulfuric acid and 1 ml of water was heated carefully until the mass began to foam. After the solution had cooled it was poured into ice water. The solid precipitate which formed was filtered off and washed with water. The yield of  $\omega$ -dodecalactam was 3.2 g. The m. p. was 151-152° on recrystallization from aqueous methanol. Published data [4]: m. p. 153-154°.

$\omega$ -Aminododecanoic acid. A solution of 1.5 g of  $\omega$ -dodecalactam and 4 g of potassium hydroxide in 25 ml of aqueous alcohol was heated for 16 hr at 150-160° in an autoclave having a capacity of 0.2 L. On completion of the heating the alcohol was distilled off, the residue diluted with water, and the aqueous solution extracted with chloroform. The alkaline solution was acidified to a weakly acidic reaction and the precipitate which formed was filtered off. The yield was 1.4 g of  $\omega$ -aminododecanoic acid which had a m. p. of 183-184° after being recrystallized from aqueous alcohol. Found: C 66.90, 66.78; H 11.69, 11.66; N 6.65, 6.59%.  $C_{12}H_{25}O_2N$ . Calculated: C 66.97; H 11.63; N 6.51%. By dissolving the  $\omega$ -aminododecanoic acid in dilute hydrochloric acid under heating, the hydrochloride of  $\omega$ -aminododecanoic acid was prepared; m. p. 163-164° (from dilute hydrochloric acid). Found: C 57.15, 57.07; H 10.42, 10.30; Cl 13.92, 14.24%.  $C_{12}H_{26}O_2NCl$ . Calculated: C 57.26; H 10.34; Cl 14.11%.

#### SUMMARY

A synthesis of  $\omega$ -aminododecanoic acid has been carried out starting with trans,trans,trans-cyclododecatriene-1,5,9.

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POLYCONDENSATION OF THE ETHYL ESTER OF GLYCINE  
IN THE PRESENCE OF ETHYL ALCOHOL

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Polycondensation of the ethyl ester of glycine in the presence of additives acting as initiators proceeds in two stages: At a definite point the rate of conversion of the aminoacid ester (i.e., the monomer) increases sharply [1]. Addition of peptide esters accelerates the polycondensation of the ethyl ester of glycine, reducing the duration of the first, slow stage. To clarify the reasons for the autocatalytic nature of this reaction, we continued investigation of the effects which the reaction products exert on the rate of polycondensation of the glycine ethyl ester. In the work described at present, the effect of ethyl alcohol which forms in the reaction was investigated. Because aliphatic alcohols accelerate the aminolysis of esters [2], it was to be assumed that ethyl alcohol would increase the rate of polycondensation of the ethyl ester of glycine.

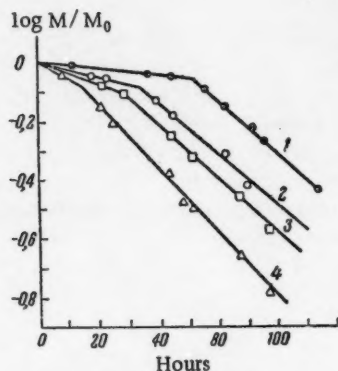


Fig. 1. Polycondensation of the ethyl ester of glycine without additives (1), in the presence of 11.5 mole% of ethyl alcohol (2), in the presence of 15 mole% of ethyl alcohol (3), and in the presence of 30% of ethyl alcohol (4).  $M/M_0$  = relative concentration of the monomer.

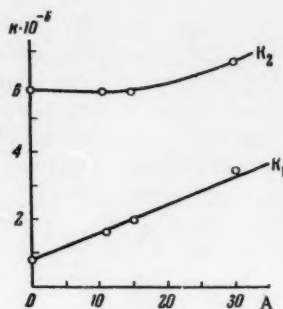


Fig. 2. Relation between the rate of conversion of the monomer and the initial concentration of ethyl alcohol:  $K_1$  and  $K_2$  - velocity constants of the conversion of the monomer in the 1st and 2nd stage of the reaction, respectively.

The kinetics of the change in the composition of the polycondensation products in the presence of 11.5\*, 15, and 30 molar % of ethyl alcohol were investigated.

As can be seen from the data given in Fig. 1 with regard to the quantity of unreacted monomer, the reaction proceeded in two stages, similarly to the already described polycondensation of the ethyl glycine ester in the absence of catalyzing additives [1]. The kinetics of the conversion of the monomer in both stages were found to

\* At the moment of the sudden increase in the rate of conversion of the monomer (in the absence of a catalyst) the quantity of ethyl alcohol that had formed amounted to 11.5 mole % with reference to the initial monomer.

correspond to those of a reaction of the first order. Addition of alcohol increased the velocity of the reaction, with the increase of velocity taking place principally in the first, slow stage of the reaction. With increasing relative concentrations of alcohol, this stage was accelerated and the time required for it shortened. The velocity constant of the conversion of the monomer in the first reaction stage was proportional to the quantity of alcohol added (Fig. 2); this relation was not found to apply to the second stage of the reaction. It follows from these results that the sharp acceleration of the reaction cannot be explained by the accumulation of alcohol at the point when the second stage of the reaction sets in. Accumulation of peptides can also not serve as an explanation for the increased rate of conversion of the monomer [1]. A comparison between the accelerating effects exerted by alcohol and peptide esters showed that alcohol has a lesser effect on the velocity of the polycondensation of the ethyl ester of glycine than an equimolar quantity of peptide esters. The effect of the quantity of alcohol added on the composition of the solid phase which formed during the polycondensation was also investigated. It was found that in polycondensations taking place in the absence of catalyzing additives the concentration of diketopiperazine in the solid phase increased somewhat as the reaction progressed.

With increased quantities of alcohol introduced into the reaction, the concentration of diketopiperazine also increased. The concentration of amino nitrogen in the products contained in the solid phase decreased as the reaction progressed, and was reduced when the quantity of alcohol added was increased. The average degree of polymerization of the peptide fraction of the reaction products did not exceed 3.5. This value dropped slightly in time. Addition of alcohol, without changing the general character of the dependence of the degree of polymerization on time, lowered the degree of polymerization, although to an insignificant extent (down to 2.9). Thus, both added alcohol and alcohol that formed during the polycondensation of the ethyl ester of glycine had the effect of increasing the formation of diketopiperazine, and of reducing to a certain extent the degree of polycondensation of the reaction products.

#### EXPERIMENTAL

Ethyl ester of glycine, which had been prepared by Fischer's method [3], was dissolved in dry ether. The resulting solution was thoroughly dried with potassium carbonate [4]. The boiling point of the glycine ethyl ester was 46-47° (10 mm). The polycondensation of the ethyl ester of glycine to which alcohol had been added, and also of the ester to which no additions of alcohol had been made, was carried out in sealed tubes at  $40^{\circ} \pm 0.2$ . Because alcohol is readily soluble in the ethyl ester of glycine, the reaction began in a homogeneous medium. The required ratio between the ethyl ester of glycine and ethyl alcohol was established by rapid weighing. The tube containing the initial reaction mixture was sealed immediately after weighing. Separation from the reaction mixture of the unreacted monomer and determination of the quantity of this monomer were carried out by a method described by us earlier [5]. The content of diketopiperazine was estimated on the basis of the increase in amino nitrogen after 20 min of hydrolysis of 0.1 N NaOH [6].

#### SUMMARY

1. The effect of ethyl alcohol on the polycondensation of the ethyl ester of glycine was investigated.
2. It was established that addition of ethyl alcohol accelerates the polycondensation in the first, slow stage of the reaction and leads to an increase in the yield of diketopiperazine.

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# APPLICATION OF THE METHOD OF CHROMATOGRAPHIC PLATES TO $\beta$ -DICARBONYL COMPOUNDS

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It has been established during the past few years [1-4] that the method of chromatographic plates can be successfully applied in the investigation of many classes of organic compounds, as for instance steroids terpenes, quinones, and carotenoids. It appeared of interest to extend the application of this method to  $\beta$ -dicarbonyl compounds in order to establish whether or not they can be separated chromatographically, and also in order to determine the relation between the  $R_f$  and the structure of these compounds. We found that if a mixture of silica gel and starch is used as the adsorbent, and the chromatographic process is conducted according to a method described by us earlier [1-4], good results are obtained with the application of the solvents benzene-ethyl acetate taken in a ratio which is varied depending on the structure of the  $\beta$ -carbonyl compound. For compounds of the aliphatic series it is best to use 7 parts by volume of benzene to 3 parts of ethyl acetate, while in the case of cyclic  $\beta$ -diketones more favorable  $R_f$  values are obtained with a 1:1 ratio of these solvents. We found that iodine vapor can be used to advantage for the development of the chromatograms.

| $\beta$ -Dicarbonyl compounds             | Ionization constants      | Volume ratio of benzene to ethyl acetate | $R_f$ |
|---|---------------------------|--|-------|
| Methylmalonic ester                       | —                         | 7:3                                      | 0.84  |
| Malonic ester                             | —                         | The same                                 | 0.76  |
| Acetoacetic ester                         | $2.1 \cdot 10^{-11}$ [16] | " "                                      | 0.59  |
| Acetylacetone                             | $1.2 \cdot 10^{-9}$ [16]  | " "                                      | 0.63  |
| 2-Formylcyclohexanone [5]                 | $4.5 \cdot 10^{-7}$ [16]  | 1:1                                      | 0.86  |
| 2-Methyldihydroresorcinol [6]             | $8.68 \cdot 10^{-7}$      | The same                                 | 0.18  |
| Indandione [7]                            | —                         | " "                                      | 0.80  |
| 2-Formylcyclopentanone                    | $1.5 \cdot 10^{-6}$ [16]  | " "                                      | 0.52  |
| Methylene bis-dimedone                    | —                         | " "                                      | 0.90  |
| Dimedone                                  | $5.6 \cdot 10^{-6}$ [16]  | " "                                      | 0.22  |
| Dihydroresorcinol                         | $0.55 \cdot 10^{-5}$ [17] | " "                                      | 0.08  |
| Tetronic acid [10]                        | $8.2 \cdot 10^{-5}$ [18]  | " "                                      | 0.21  |
| 2-Bromodihydroresorcinol [11]             | —                         | " "                                      | 0.27  |
| 2-Prenyldihydroresorcinol [12]            | —                         | " "                                      | 0.40  |
| 2-Bromodimedone [13]                      | —                         | " "                                      | 0.44  |
| 2-Allyldihydroresorcinol [14]             | —                         | " "                                      | 0.27  |
| 2-Carboethoxymethyldihydroresorcinol [15] | —                         | " "                                      | 0.11  |

The experiments which were carried out (cf. table) indicated that in some cases there is an inverse correlation between the  $R_f$  and the acidity of  $\beta$ -dicarbonyl compounds, although the exceptions which have been found, for instance in the cases of acetylacetone and acetoacetic ester, preclude a conclusion in regard to the existence of any generally valid relation. The high  $R_f$  values found for substituted dihydroresorcinols, including methylene bis-dimedone, are noteworthy.

Examples of the separation of  $\beta$ -dicarbonyl compounds (solvents, benzene: ethyl acetate = 1:1).



Fig. 1.

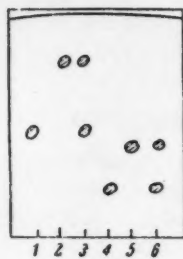


Fig. 2.

Fig. 1. 1) Dihydroresorcinol; 2) dimedone; 3) dihydroresorcinol + dimedone.

Fig. 2. 1) 2-Formylcyclopentanone; 2) 2-formylcyclohexanone; 3) 2-formylcyclopentanone + 2-formylcyclohexanone; 4) bromodihydroresorcinol; 5) bromodimedone; 6) bromodihydroresorcinol + bromodimedone.

In conclusion we would like to express our thanks to E. Lederer for the interest evinced towards the work described in this instance.

#### SUMMARY

The chromatographic behavior of  $\beta$ -dicarbonyl compounds was investigated using as an adsorbent silica gel - starch fastened to a glass plate.

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# FACTORS WHICH BRING ABOUT A CHANGE IN THE MECHANISMS OF CARBON FORMATION IN CONNECTION WITH THE DECOMPOSITION OF HYDROCARBONS

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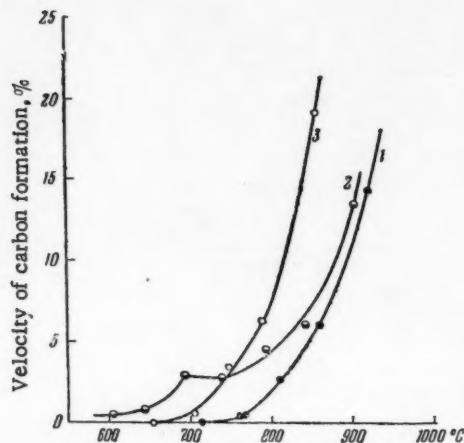
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As had been established earlier [1, 2], during the decomposition of various hydrocarbons (alkylbenzenes, naphthenes, and normal paraffins with 6 or 7 carbon atoms) on silica gel, several different mechanisms of carbon formation are observed, which is expressed in sharp changes taking place in the uniform course of velocities of carbon formation following a temperature increase. Several mechanisms of carbon formation have also been observed in connection with the catalytic decomposition of alcohols [3, 4]. In all cases investigated by us the mechanisms of carbon formation involved polycondensation of the initial organic substances or of some preliminary products of their transformation, while the exchange mechanisms consisted in the replacement of one carbon-forming material with another. For instance, in the case of alkylbenzenes the low-temperature mechanism of carbon formation involved polycondensation of the initial hydrocarbons over the alkyl groups, whereas the high-temperature mechanism comprised polycondensation of the fully or partly desalkylated alkylbenzenes by the formation of bonds between the nuclei [1]; in the case of naphthenes and normal paraffins with 6 or 7 carbon atoms, the low-temperature mechanism consisted of a polycondensation of olefins, while the high-temperature mechanism involved polycondensation of lower paraffins and of aromatic hydrocarbons which had formed earlier from the initial substances [2]. In the case of alcohols the low-temperature mechanism was found to represent a polycondensation of aldehydes and ketones, the intermediate mechanism a polycondensation of olefins, and the high-temperature mechanism a polycondensation of the simplest paraffins and of aromatic hydrocarbons that had formed as a result of the decomposition of the initial alcohols [3-6].



Dependence of velocities of carbon formation on the temperature in the decomposition of methane (1), n-pentane (2), and benzene (3) on silica gel.

of the decomposition of the simplest paraffinic hydrocarbon, methane, one might expect that the same mechanism of carbon formation would be observed in the 700-1000° temperature range, because no modification of the carbon-forming material consisting of methane can take place here as a result of a simplification of the molecule of this substance.

To check the correctness of this assumption, an investigation was carried out of the carbon formation taking place in connection with the decomposition of methane and, for comparison purposes, in connection with the

decomposition of benzene and n-pentane under identical conditions on KSM silica gel, employing a method that has been developed earlier [1, 2, 7]. The volume of the catalyst was 5 ml; the rate at which the reacting substances were supplied 0.05 M/hr. As can be seen from the figure, the velocity of carbon formation from methane, just as in the case of benzene, increased smoothly with the temperature. There are no breaks in the curve expressing the relation of the velocity of carbon formation to the temperature in the case of either methane or benzene. On the other hand, such breaks can be clearly observed in the case of n-pentane. In work conducted earlier [1-4] breaks in the uniform course of the velocity of carbon formation were always found to be associated with changes in the mechanism of carbon formation. Consequently, in the case of carbon formation during the decomposition of methane, where no such breaks occur, we actually have, as has been assumed above, only one mechanism of carbon formation throughout the entire temperature range investigated. The process of carbon formation from methane apparently consists of a multistage dehydrocondensation of the initial methane with polycyclic aromatic hydrocarbons that form in part as a result of the decomposition of methane (see Table 1). Individual molecules of these hydrocarbons become nuclei for macromolecules of carbonaceous matter by progressively growing, as a result of numerous acts of dehydrocondensation with methane, into polycyclic condensed hydrocarbons, i.e., carboids. In this case the initial methane functions directly as the carbon-forming material. There are no reasons to believe that resins play a significant role as a carbon-forming material, because the extent of the formation of resins in the decomposition of methane was low as compared with the formation of carbonaceous matter (see Table 1).

TABLE 1. Quantity of Resin\* Formed Expressed in % of Introduced Hydrocarbon

| Hydrocarbon | 650° | 700° | 750° | 800° | 850° | 900° | 950° |
|-------------|------|------|------|------|------|------|------|
| Benzene     | 3,1  | 6,3  | 12,1 | 22,6 | 11,0 | —    | —    |
| n-Pentane   | 0,8  | 1,7  | 6,0  | 7,0  | 8,7  | 8,2  | —    |
| Methane     | 0,0  | 0,0  | 0,1  | 0,2  | 0,3  | 0,5  | 0,6  |

\* The resinous products of condensation consist of a mixture of aromatic hydrocarbons. In the case of benzene they are composed essentially of diphenyl. In other cases a considerable quantity of naphthalene was found in the resin.

TABLE 2. Composition of Contact Gases Formed in the Decomposition of Benzene, n-Pentane, and Methane on Silica Gel

| Hydrocarbon | Temp.,<br>in °C | Composition of contact gases in volume % |                 |                               |                               |                   |                               |
|-------------|-----------------|--|-----------------|-------------------------------|-------------------------------|-------------------|-------------------------------|
|             |                 | H <sub>2</sub>                           | CH <sub>4</sub> | C <sub>2</sub> H <sub>6</sub> | C <sub>2</sub> H <sub>4</sub> | higher<br>olefins | C <sub>2</sub> H <sub>2</sub> |
| Benzene     | 824             | 100                                      | 0               | 0                             | 0                             | —                 | 0                             |
|             | 902             | 100                                      | 0               | 0                             | 0                             | —                 | 0                             |
| n-Pentane   | 645             | 10                                       | 20              | 10                            | 36                            | 24                | —                             |
|             | 743             | 26                                       | 40              | 15                            | 12                            | 7                 | —                             |
| Methane     | 750             | 6  | 91              | 1,5                           | 3                             | —                 | 0                             |
|             | 850             | 12                                       | 83              | 2                             | 2                             | —                 | Traces                        |
|             | 950             | 29                                       | 63              | 4                             | 0                             | —                 | 8                             |

During the decomposition of n-pentane there was apparently a change in the mechanism of carbon formation at 690-750°. The high-temperature mechanism in this case apparently involved polycondensation of saturated products which formed as a result of pentane decomposition, and consisted principally of methane, because at temperatures above 850° the velocity of carbon formation from pentane approached the corresponding velocity values for methane (see Fig. 1), while in the contact gases there was an increasing content of methane, which comprised the major portion of the hydrocarbon content of the gas (Table 2). At temperatures from 750 to 850° aromatic resinous

substances which had formed earlier from n-pentane began to play a principal role as carbon-forming materials. This was indicated by a reduction in the rate of increase of their formation at temperatures above 750° (see Table 1), a phenomenon which apparently was due to the fact that these substances were used up in the process of carbon formation. On transition to the high-temperature mechanism of carbon formation, there was a sharp decrease in the content of unsaturated substances in the contact gases (Table 2). One must therefore assume that olefins which originally formed as a result of the cracking of the initial hydrocarbons functioned as the carbon-forming material in the stage when the low-temperature mechanism of carbon formation was active.

#### SUMMARY

It was established that the number of possible mechanisms of carbon formation in the decomposition of hydrocarbons of various types or of other organic substances is determined by the number of carbon-forming materials of different chemical types which may arise under the conditions under which the initial substance is decomposed.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

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# INFRARED ABSORPTION SPECTRA OF MONO- AND DIACYLATED THIOPHENE HOMOLOGS

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Thiophene derivatives to which one or two carbonyl groups are attached are of interest from the standpoint of the investigation of the problem in regard to the effect which the position and nature of substituents exert on the conjugation of carbonyl groups with the double bond system of the thiophene ring. Some information on the conjugation can be obtained by studying the frequencies and total absolute intensities of bands of infrared absorption by groups that are conjugated with the aromatic ring. Lowering of the frequency, which is accompanied by a simultaneous increase of the intensity of absorption bands, indicates an increased degree of conjugation. A number of benzene derivatives have been investigated from this standpoint [1]. It was of interest to compare data obtained for benzene derivatives with data derived from the study of other aromatic systems, such as that of the type of thiophene, which contains an atom with an unshared electron pair and has a structure different from that of benzene as far as its geometry is concerned [2].

## EXPERIMENTAL

The thiophene derivatives subjected to spectrometric investigation, both those prepared for the first time by Gol'dfarb and one of the authors of this article [3], and those described earlier, were purified thoroughly by multiple fractional distillation in vacuum in a stream of dry argon, and in the case of crystalline substances, by multiple recrystallization followed by fractional sublimation in vacuum at 2 mm. The infrared spectra in the region of absorption by the C=O bond were determined on an IKS-14 instrument equipped with a NaCl prism. The spectral width of the slit was approximately  $11\text{ cm}^{-1}$ . KBr cuvettes with a thickness of 0.01 cm were used. The solvents used were  $\text{CHCl}_3$  and  $\text{CCl}_4$ . The precision of the determination of frequencies was  $\pm 3\text{ cm}^{-1}$ . The total absolute intensity of the C=O band was determined by Bourgin's method as modified and improved by Ramsay [4]. The values of total absolute intensities are given in  $1 \cdot 10^{-4} \text{ M}^{-1} \cdot \text{l} \cdot \text{cm}^{-2}$  with a precision of  $\pm 0.1 \cdot 10^{-4}$ . The data on the frequencies of C=O groups in aliphatic compounds, benzene derivatives, and thiophene derivatives are listed in Table 1.

TABLE 1. Comparison of the Frequencies of C=O Groups in Different Types of Compounds

| Name of compound                            | Frequency of the C=O<br>in $\text{cm}^{-1}$ ( $\text{CCl}_4$ solution) |
|---|--|
| Methyl ester of acetic acid                 | 1750 [5]   |
| Methyl ester of benzoic acid                | 1725 [6]   |
| Methyl ester of thiophene-3-carboxylic acid | 1727   |
| Methyl ester of thiophene-2-carboxylic acid | 1724   |

In the case of the methyl ester of benzoic acid conjugation of the C=O group with the benzene ring resulted in a lowering of the frequency by  $25\text{ cm}^{-1}$ , whereas the frequency of the C=O group in the  $\beta$ -position of the thiophene ring was lowered by  $23\text{ cm}^{-1}$  as compared with the methyl ester of acetic acid. When the C=O group was in the  $\alpha$ -position, the frequency was still lower, a phenomenon which has also been observed in other compounds [7]. This is in accordance with the fact that the conjugation of a C=O group in an  $\alpha$ -position is stronger than that of a C=O group in a  $\beta$ -position. We find a confirmation for this in ultraviolet spectroscopy data [8].

When two  $\alpha$ -acetyl groups were present (see Table 2), the frequency of the C=O groups was markedly higher than that of a single acetyl group in an  $\alpha$ -position, while the intensity of absorption by these groups was lower than the intensity of a single group multiplied by two. This is apparently due to the competition between two electro-negative groups.

TABLE 2. Frequencies, Total Absolute Intensities, and Angles of Emergence of C=O Groups

| Name of compound  | $\nu$ in $\text{cm}^{-1}$ , solvent $\text{CHCl}_3$ | $A(\text{C=O})$ $1 \cdot 10^4 \cdot \text{M}^{-1}$ $\text{L} \cdot \text{cm}^{-2}$ | $\theta$ in degrees |              |
|---|---|--|---------------------|--------------|
|   |   |  | $\alpha$            | $\beta$      |
| 2-Methyl-5-acetothienone  | 1660  | 2,8  | 10                  |              |
| 2,5-Dimethyl-3-acetothienone                                    | 1672  | 2,3  |                     | 50           |
| 2,5-Dimethyl-3-ethyl-4-acetothienone                            | 1676  | 2,6  |                     | 50           |
| 2,5-Di-tert-butyl-3-acetothienone                               | 1684  | 2,2  |                     | 50           |
| 2-Bromo-5-acetothienone   | 1665  | 2,7  | 10                  |              |
| 5-Methyl-2,4-diacetylthiophene                                  | 1676  | 5,3  | 10                  | 50           |
| 2,5-Diacetylthiophene   | 1684  | 4,7  | 10                  |              |
| Methyl ester of thiophene-2-carboxylic acid                     | 1710  | 3,8  | 0-180               |              |
| Methyl ester of thiophene-3-carboxylic acid                     | 1714  | 3,1  |                     | 0-180        |
| Dimethyl ester of 5-methylthiophene-2,4-dicarboxylic acid       | 1716  | 7,1  | 0-180               | 40           |
| Dimethyl ester of 2,5-dimethylthiophene-3,4-dicarboxylic acid   | 1726  | 8,1  | $\beta_1$ 40        | $\beta_2$ 40 |
| Ethyl ester of 2,5-dimethyl-4-acetylthiophene-3-carboxylic acid | 1708  | 6,0  | 50                  | 40           |

Introduction of a bromine atom into the  $\alpha$ -position did not result in a significant change in the frequency or intensity, as has been observed in the case of benzene derivatives [9].

For a number of molecules in which the carbonyl groups emerge from the plane of the thiophene ring because of steric hindrance, the angles of emergence of the carbonyl groups have been calculated in an approximate manner. It was assumed for the purpose of the calculation that the forces which are active between atoms that are not linked to each other by valency bonds can be described by the expression for the Lennard-Jones potential:

$$V(r) = \frac{A}{r^{12}} - \frac{B}{r^6}; A = V_0(r_0)^{12}; B = 2V_0(r_0)^6$$

where  $r_0$  is the sum of the van der Waals radii of the interacting atoms, while the forces of conjugation can be described by an expression for a potential of the type  $V(\theta) = c |\cos \theta|$ , where  $\theta$  is the angle of emergence from the plane of the ring. It was tentatively assumed that  $V_0 = 1 \text{ kcal/M}$  and  $C = 5 \text{ kcal/M}$ . The conclusions made in regard to the change of conjugation with the magnitude of the angle of emergence of the C=O group from the plane of the ring, based on values for the angle calculated from the  $V_0$  and  $C$  values given above, were qualitatively in good agreement with conclusions in regard to conjugation made on the basis of frequency and intensity data. However, in the limiting case of  $\theta = 90^\circ$ , the frequency of the C=O group did not reach the value for the frequency corresponding to an aliphatic ketone, but was increased by approximately one half of the difference between the frequencies of a C=O group in an aliphatic ketone and a C=O group located in the plane of a thiophene ring. This is difficult to explain, because there are many factors which affect the frequency and intensity of a C=O group. The presence of two -COOR or -COR groups in  $\beta$ -positions does not result in an increase of the angle of emergence of the C=O group from the plane of the thiophene ring. One may conclude from this that a second acetyl group can be introduced with relative ease into a  $\beta$ -position, as has been demonstrated experimentally by Gol'dfarb and one of the authors of this article [3].

#### SUMMARY

1. The frequencies and total absolute intensities of the infrared spectrum absorption band of the C=O groups were determined for a number of mono- and diacylated thiophene homologs and esters of thiophene mono- and dicarboxylic acids.

2. An approximate calculation was made of the angles of emergence of C=O groups from the plane of the thiophene ring.

3. The frequencies and total absolute intensities of C=O groups were correlated with the position and nature of the substituent groups.

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## INHIBITORS OF FREE-RADICAL REACTIONS

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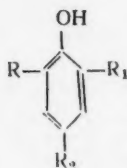
Translated from *Izvestiya Akademii Nauk SSSR, Otdeleniye Khimicheskikh Nauk*,

No. 1, pp. 168-170, January, 1961

Original article submitted July 7, 1960

Recently, inhibitors of free-radical reactions have begun to acquire increasing importance in different branches of chemistry, in chemical technology, in the food industry, and in other technical fields. It was demonstrated a short time ago in work done by Emanuel' and his collaborators that substances of this class are capable of inhibiting some enzymatic processes and that they may therefore be of interest as drugs which suppress the growth of malignant tumors [1-3]. At the suggestion of Emanuel', we started from this standpoint systematic research on the synthesis of inhibitors of free-radical processes. The work described in this instance deals with the synthesis of some new compounds which belong to the class of screened phenols.

It is known that screened phenols of the general formula



where R, R<sub>1</sub>, and R<sub>2</sub> are alkyls, are used extensively as antioxidants [4-8]. The inhibiting activity of the screened phenols depends to a considerable extent on the ortho-substituents and their structure; it increases with the degree of branching of these substituents. The para-substituent exerts a less pronounced effect [9]. Thus, in the series of the three compounds 2,4,6-trimethylphenol, 2,6-diisopropyl-4-methylphenol, and 2,6-di-tert-butyl-4-methylphenol (ionol) the index of inhibiting activity increases with the increase in the length of the ortho-substituent and has the highest value in the case of the last of the three compounds [10]. Starting from this, it appeared of interest to prepare a number of screened phenols with a structure based on that of p-cresol. In the work reported here we synthesized a number of homologs of ionol with ortho-substituents ranging from C<sub>5</sub> to C<sub>8</sub>. We employed for their synthesis one of the most thoroughly developed methods, i.e., that of the alkylation of p-cresol with olefins [11].

By the action of appropriate alkylmagnesium halides on acetone, tertiary alcohols were prepared which were then dehydrated to the corresponding olefins by heating with sulfuric acid. The alkylation took place in several hours when the olefin was added at 65-70° to a mixture of p-cresol and a quantity of sulfuric acid sufficient to exercise a catalytic effect. The unreacted p-cresol and the monoalkylate were separated by treatment with an aqueous alcoholic solution of caustic alkali. The polymers which formed from the olefins were eliminated by fractionation through a column. The quinoids, which are difficult to separate, were removed by recrystallization from alcohol or by chromatography with the use of a column filled with silica gel. Figure 1 shows the infrared spectra which were obtained with 5% solutions in carbon tetrachloride of the substances prepared. As was to be expected, the absorption curves lie very close to each other and differ only with respect to the intensity of the CH<sub>2</sub> group bands. Comparison of the 2800-3050 cm<sup>-1</sup> regions shows clearly the increase of the number of methylene groups in the ortho-substituents. The table lists the physical constants of the compounds synthesized, and, specifically, gives a value which characterizes their inhibiting properties. As a measure of the effectiveness of the inhibitors (ε) a value was selected which expresses the ratio of the length of the induction period of the oxidation of molten lard in the presence of the inhibitor to the length of the induction period in the presence of ionol, an inhibitor the activity

| Name of compound                              | R = R <sub>2</sub>   | R <sub>1</sub>   | Analysis, % |       |       |       | M.p., °C | B. P., °C<br>(P, mm Hg) | d <sub>4</sub> <sup>20</sup> | n <sub>D</sub> <sup>20</sup> | MR     |        | Yield,<br>% |      |
|---|--|------------------|-------------|-------|-------|-------|----------|-------------------------|------------------------------|------------------------------|--------|--------|-------------|------|
|   |  |                  | found       | calc. | found | calc. |          |                         |                              |                              |        |        |             |      |
| 2,6-Di-(1',1'-di-methylpropyl)-4-methylphenol | $\begin{array}{c} \text{CH}_3 \\   \\ -\text{C}-\text{CH}_2\text{CH}_3 \\   \\ \text{CH}_3 \\   \\ \text{CH}_3 \end{array}$              | —CH <sub>3</sub> | 81,88       | 82,19 | 11,11 | 11,36 | 5,5—6    | 146—148 (8)             | 0,9386                       | 1,5098                       | 79,12  | 78,63  | 1,14        | 62   |
| 2,6-Di-(1',1'-di-methylbutyl)-4-methylphenol  | $\begin{array}{c} \text{CH}_3 \\   \\ -\text{C}-\text{CH}_2\text{CH}_2\text{CH}_3 \\   \\ \text{CH}_3 \end{array}$                       | —CH <sub>3</sub> | 82,25       | 82,54 | 11,66 | 11,67 | 44—45    | 154—159 (7)             | —                            | —                            | —      | —      | 0,92        | 19,7 |
| 2,6-Di-(1',1'-di-methylamyl)-4-methylphenol   | $\begin{array}{c} \text{CH}_3 \\   \\ -\text{C}-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \\   \\ \text{CH}_3 \end{array}$            | —CH <sub>3</sub> | 82,20       | 82,82 | 11,86 | 11,91 | 27,5—28  | 171—173 (7)             | —                            | —                            | —      | —      | 1,04        | 18,5 |
| 2,6-Di-(1',1'-di-methylhexyl)-4-methylphenol  | $\begin{array}{c} \text{CH}_3 \\   \\ -\text{C}-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \\   \\ \text{CH}_3 \end{array}$ | —CH <sub>3</sub> | 82,86       | 83,06 | 12,18 | 12,12 | —        | 192—194 (10)            | 0,9191                       | 1,4975                       | 106,00 | 106,30 | 0,97        | 16,2 |

of which is taken as a standard. The inhibitor concentration used was 0,009 mM/g of iard. The tests on the comparative effectiveness of the inhibitors were conducted by Ter-Vartanyan, Shershavova, and Solov'eva. All substances



Infrared spectra of the compounds synthesized: 1) 2,6-di-(1',1'-dimethylpropyl)-4-methylphenol; 2) 2,6-di-(1',1'-dimethylbutyl)-4-methylphenol; 3) 2,6-di-(1',1'-dimethylamyl)-4-methylphenol; 4) 2,6-di-(1',1'-dimethylhexyl)-4-methylphenol.

synthesized were found to have an index of inhibiting activity of the same order of magnitude: There was no significant increase with the increase in the length of the ortho-substituents. However, the higher stability of 2,6-di-(1',1'-dimethylpropyl)-4-methylphenol when exposed to the action of the air, and the greater solubility of this compound are evidently of interest from the physiological standpoint. The lower yield of screened phenols with  $C_6 - C_8$  ortho-substituents as compared with their homologs with  $C_4 - C_5$  substituents can apparently be explained by the greater tendency of  $C_6 - C_8$  olefins to form polymers. Because this question was beyond the scope of the problem to be solved, and also in view of the fact that the activity of the substances synthesized was of the same order of magnitude as that of ionol, no special investigation aimed at an improvement of the yields was undertaken.

#### EXPERIMENTAL

**2,6-Di-(1',1'-dimethylpropyl)-4-methylphenol.** Thirty g of p-cresol and 1.5 ml of sulfuric acid (sp.g. 1.83) were heated to 70°, whereupon 50.6 g of iso-amylenes (b. p. 35-38°) was added dropwise to the mixture within 2 hr. After this the mixture was agitated at 65-70° for an additional period of 3 hr. After the mixture had been cooled, 300 ml of ether was added to it. The ethereal solution was successively washed with 50 ml of water, 50 ml of Claisen solution (100 g of caustic alkali in 125 ml of water and 375 ml of methanol), and 100 ml of water, whereupon it was dried. On evaporation of the solvent the residue was subjected to fractional distillation and the fraction with the b. p. 146-148° (7 mm) collected; yield 42.8 g (62%).

The other screened phenols were prepared similarly; the results obtained are listed in the table. The authors express their thanks to N. M. Emanuel' for suggesting the subject of the investigation and for the interest which he evinced towards the work that has been carried out.

#### SUMMARY

1. A synthesis of four 2,6-di-tert-alkyl-4-methylphenols has been carried out.
2. In the series of compounds synthesized, lengthening of the carbon chain of the ortho-substituents was not found to exert a significant effect on the index of inhibiting (antioxidant) activity.

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# THE SYNTHESIS OF 3,5-DI-TERT-BUTYL-4-HYDROXYBENZYLAMINE AND 3,5-DI-(1',1'-DIMETHYLPROPYL)-4-HYDROXYBENZYLAMINE

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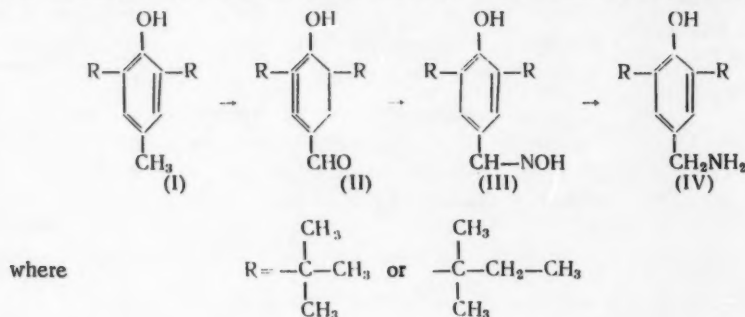
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The use of ionole (2,6-di-tert-butyl-4-methylphenol) as an inhibitor for free radical processes for suppressing malignant neoplasms in animals has shown its effectiveness [1]. At the same time a difficulty with ionole is the need for using its oil solutions in biological experiments. In order to widen the sphere of use of screening phenols in the biological field, Émanuél' suggested undertaking the synthesis of compounds which, with the structure of screening phenols, would also be water soluble. We have previously described [2] screening phenols which are homologs of ionole with long carbon chains from  $C_5$  to  $C_8$  as ortho substituents. These substances have an inhibitory index  $\epsilon$  of the same order as ionole, with some deviation in the case of 2,6-di-(1',1'-dimethylpropyl)-4-methylphenol, but they are soluble only in peach and apricot oils and organic solvents.

The present work is devoted to the synthesis of water soluble analogs of ionole with amino substituents in the methyl group. As the starting substances we took ionole and 2,6-di-(1',1'-dimethylpropyl)-4-methylphenol.



As this scheme shows, the intermediate product in the synthesis of 3,5-di-tert-butyl-4-hydroxybenzylamine (IV) was the known [3] aldehyde (II) formed in the successive bromination and hydrolysis of the corresponding alkylphenol (I). Reduction of the oxime of aldehyde (II) with zinc dust in acetic acid or catalytically over palladium black gave the benzylamine (IV). Its salts were sufficiently soluble in water. By this scheme, using 2,6-di-(1',1'-dimethylpropyl)-4-methylphenol as the starting compound, we obtained the second base.

## EXPERIMENTAL

3,5-Di-tert-butyl-4-hydroxybenzaldehyde was obtained by the method of Coppinger [3], yield 85.3% of the theory; m. p. 187-188°

3,5'-Di-(1',1'-dimethylpropyl)-4-hydroxybenzaldehyde. We heated 2.3 g (0.009 M) of 2,6-di-(1',1'-dimethylpropyl)-4-methylphenol, 46 ml of glacial acetic acid, and 11.5 ml of water to 40°. To the mixture we added 0.95 ml (0.018 M) of bromine, kept it at 40° for 2 hr, cooled it and added 10 ml of water. The yellow, crystalline aldehyde was separated, washed with water, and dried. Yield 1.75 g (71.6%); m. p. 115-115.5° (from methanol). Found: C 77.26; H 9.95%.  $C_{17}H_{26}O_2$ . Calculated: C 77.80; H 9.98%.

3,5-Di-tert-butyl-4-hydroxybenzaldoxime [(III),  $R = -C(CH_3)_3$ ]. Five g (0.020 M) of aldehyde [(II),  $R = C(CH_3)_3$ ], 1.6 g (0.023 M) of hydroxylamine hydrochloride, five g (0.125 M) of sodium hydroxide and 75 ml of water were shaken for 6 hr. The unreacted aldehyde was separated, and the mother liquor was saturated with carbon dioxide gas. The oxime which precipitated was filtered off and dried. Yield 3.1 g (88.1%); m. p. 131-132° (from benzene). Found: N 5.34, 5.31%.  $C_{15}H_{23}O_2N$ . Calculated: N 5.62%. In an analogous way we obtained 3,5-di-(1',1'-dimethylpropyl)-

hydroxybenzaldehyde [(III),  $R = -C(CH_3)_2CH_2CH_3$ ], yield 90.3% of the theory; m. p. 124-125.5° (from benzene). Found: C 73.63, 73.73; H 9.30, 9.54; N 5.15, 5.12%.  $C_{17}H_{27}O_2N$ . Calculated: C 73.60; H 9.81; N 5.05%.

3,5-Di-tert-butyl-4-hydroxybenzylamine [(IV),  $R = C(CH_3)_3$ ]. a) To a mixture of 20.7 g (0.32 M) of zinc dust, 0.3 g of copper sulfate, and 400 ml of 35% acetic acid at 96-100° was added 23.7 g (0.095 M) of oxime in 100 ml of 75% acetic acid. After keeping the mixture for 3 hr, it was cooled, poured into 100 ml of water, and filtered; the mother liquor was made alkaline with 40% sodium hydroxide solution. The base was extracted with ether, the extract was dried, and the ether was removed. Yield 16.8 g (74.6%); m.p. 158-159° (from benzene).

b) Sixteen g (0.064 M) of oxime in 250 ml of glacial acetic acid and 2 ml of sulfuric acid (sp. gr. 1.83) was hydrogenated in the presence of 2 g of palladium black at room temperature and normal pressure. The catalyst was separated, the acetic acid was distilled off, the residue was dissolved in the minimum amount of water and filtered; the mother liquor was made alkaline with aqueous ammonia. The precipitate of base was separated and dried. Yield 13.2 g (87.4%); m. p. 157.5-158.5° (from benzene). Found: N 5.81, 5.69%.  $C_{15}H_{25}ON$ . Calculated: N 5.95%. Hydrochloride white needles, m. p. 217.5-218° (from water). Hydrobromide, white needles, m. p. 241.5-242° (from water). Found: C 56.96, 56.97; H 8.42, 8.51; N 4.40, 4.50; Br 25.22, 25.05%.  $C_{15}H_{26}ONBr$ . Calculated: C 56.98; H 8.29; N 4.42; Br 25.25%. Ascorbate, white leaflets, m. p. 142-144° (with decomposition). Acetyl derivative, m. p. 130-131° (from alcohol), phthalyl derivative, m. p. 173.5-174.5° (from alcohol).

3,5-Di-(1',1'-dimethylpropyl)-4-hydroxybenzylamine was obtained by hydrogenation over palladium black under analogous conditions. Yield 90.7%; m. p. 95-96° (from hexane). The hydrochloride has m. p. 211.5-212° (from water); hydrobromide, m. p. 225-226° (from water). Found: N 4.07, 4.21; Br 23.17, 23.36%.  $C_{17}H_{30}ONBr$ . Calculated: N 4.07; Br 23.20%.

The authors thank N. M. Émanuël' for suggesting this study and for interest in the work.

#### SUMMARY

1. We have synthesized water soluble analogs of ionole: 3,5-di-tert-butyl-4-hydroxybenzylamine and 3,5-di-(1',1'-dimethylpropyl)-4-hydroxybenzylamine.

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THE IDENTIFICATION OF  $\alpha, \alpha, \alpha, \omega$ -TETRACHLOROALKANES  
AND  $\alpha, \beta$ -UNSATURATED  $\alpha, \alpha, \omega$ -TRICHLOROALKENES BY  
THE PICRATES OF THEIR ISOTHIURONIUM DERIVATIVES

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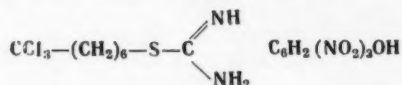
Original article submitted June 10, 1960

Salts of isothiuronium derivatives are widely used for identification of alkyl halides [1-5]. S-Alkylisothiuronium derivatives which contain halogens in the alkyl group are very little known [10]. Picrates have been obtained from isothiuronium derivatives, starting from compounds of the structure  $\text{HCCl}_2-\text{CClH}-\text{CH}_2\text{Br}$  and  $\text{CH}_2\text{Cl}-\text{CHCl}-\text{CH}_2\text{Br}$ , in which only bromine is replaced by the isothiuronium residue; in compounds of the structure  $\text{CCl}_2=\text{CCl}-\text{CH}_2\text{Cl}$ ,  $\text{CH}_2=\text{CCl}-\text{CH}_2\text{Cl}$  and  $\text{CHCl}=\text{CH}-\text{CH}_2\text{Cl}$  the allyl atom of chlorine is easily replaced by the isothiuronium group [6, 7]. There have also been syntheses of a series of picrates of isothiuronium derivatives which contain fluorine and chlorine in the alkyl groups [8]. Such compounds are obtained by replacement of the bromine by the isothiuronium group in the compounds  $\text{CFCI}_2-\text{CH}_2-\text{CH}_2\text{Br}$  and  $\text{CFCIH}-\text{CHCl}-\text{CH}_2\text{Br}$ , and also by replacement of the allyl chlorine in the compound  $\text{CFCI}=\text{CH}-\text{CH}_2\text{Cl}$ .

In the present work we describe the preparation of picrates of isothiuronium derivatives starting from  $\alpha, \alpha, \alpha, \omega$ -tetrachloroalkanes and  $\alpha, \alpha, \omega$ -trichloroalkenes. By the action of thiourea on  $\alpha, \alpha, \alpha, \omega$ -tetrachloroalkanes the isothiuronium group replaces the chlorine only in the chloromethyl group. The trichloromethyl group in accordance with the generally observed rule [9] remains inert to the action of nucleophilic reagents. The reaction with  $\alpha, \alpha, \omega$ -trichloroalkenes takes place in an analogous way. The isothiuronium derivatives are formed in good yields; their picrates are purified by recrystallization from alcohol. The resulting picrates have characteristic and sufficiently high melting points, and can be used for the purpose of identification.

# EXPERIMENTAL

## Preparation of S-(7,7,7-trichloro-n-heptyl)-isothiuronium picrate,



In a glass ampule we placed 3.57 g of 1,1,1,7-tetrachloroheptane, 1.14 g of thiourea, and 2.49 g of potassium iodide in 10 ml of acetone. The sealed ampule was heated on a boiling water bath for 18 hr. After cooling, the ampule was opened, the precipitate which had formed was filtered off and carefully washed with acetone. The filtrate and acetone solution were combined and evaporated in a vacuum. The residue was dissolved in alcohol and treated with excess picric acid. For full precipitation of S-(7,7,7-trichloroheptyl)isothiuronium picrate the reaction mixture was diluted with a small amount of water. The yield of picrate was nearly quantitative, m. p. 185-185.6° (after three recrystallizations from alcohol).

The other picrates were obtained in an analogous way. Usually the reaction was carried out with 0.015 M of polyhalogen derivative and an equimolecular amount of potassium iodide and thiourea. The picrates were recrystallized to constant melting point of the sample. The results are given in Tables 1 and 2.

TABLE 1. Picrates with Structure  $\text{CCl}_3-(\text{CH}_2)_n-\text{S}-\text{C} \begin{smallmatrix} \text{NH} \\ \text{NH}_2 \end{smallmatrix} \text{C}_6\text{H}_2(\text{NO}_2)_3\text{OH}$

| n  | M.p., °C  | Found, % |      |       |       | Calculated, % |      |       |       |
|----|-----------|----------|------|-------|-------|---------------|------|-------|-------|
|    |           | C        | H    | N     | Cl    | C             | H    | N     | Cl    |
| 4  | 150—150,5 | 30,54    | 3,01 | 14,53 |       | 30,09         | 2,92 | 14,62 |       |
|    |           | 30,58    | 2,91 | 14,56 |       |               |      |       |       |
| 6  | 185—185,5 | 38,17    | 3,51 | 14,00 | 20,75 | 33,16         | 3,52 | 13,82 | 21,02 |
|    |           | 33,10    | 3,52 | 14,14 | 20,56 |               |      |       |       |
| 8  | 147—148   | 35,73    | 4,13 | 13,21 | 19,84 | 35,92         | 4,11 | 13,09 | 19,92 |
|    |           | 35,79    | 4,16 | 13,19 | 19,69 |               |      |       |       |
| 10 | 142—143,5 | 38,46    | 4,30 | 12,57 |       | 38,47         | 4,66 | 12,46 |       |
|    |           | 38,45    | 4,36 |       |       |               |      |       |       |
| 12 | 138—140   | 40,58    | 5,11 | 12,07 |       | 40,81         | 5,08 | 11,85 |       |
|    |           | 40,44    | 5,19 |       |       |               |      |       |       |

TABLE 2. Picrates with Structure  $\text{CCl}_2=\text{CH}(\text{CH}_2)_n-\text{S}-\text{C} \begin{smallmatrix} \text{NH} \\ \text{NH}_2 \end{smallmatrix} \text{C}_6\text{H}_2(\text{NO}_2)_3\text{OH}$

| n  | M.p., °C  | Found, % |      |       |       | Calculated, % |      |       |       |
|----|-----------|----------|------|-------|-------|---------------|------|-------|-------|
|    |           | C        | H    | N     | Cl    | C             | H    | N     | Cl    |
| 3  | 123—124   | 32,13    | 2,90 |       | 16,67 | 32,57         | 2,94 |       | 16,06 |
|    |           | 32,03    | 2,89 |       | 16,39 |               |      |       |       |
| 5  | 163—165   | 35,84    | 3,52 |       |       | 35,74         | 3,61 |       |       |
|    |           | 35,57    | 3,45 |       |       |               |      |       |       |
| 7  | 151,5—153 | 38,87    | 4,28 | 14,44 | 13,79 | 38,55         | 4,21 | 14,05 | 14,25 |
|    |           | 38,59    | 4,13 | 14,38 | 13,70 |               |      |       |       |
| 9  | 143—144   | 41,33    | 4,95 |       | 13,47 | 41,07         | 4,75 |       | 13,51 |
|    |           | 41,50    | 5,11 |       | 13,18 |               |      |       |       |
| 11 | 133—134   | 42,67    | 5,11 | 12,63 |       | 43,31         | 5,23 | 12,63 |       |
|    |           | 42,54    | 4,95 | 12,60 |       |               |      |       |       |
| 13 | 126—127   | 45,08    | 5,44 |       |       | 45,35         | 5,67 |       |       |

#### SUMMARY

1. Starting from  $\alpha, \alpha, \alpha, \omega$ -tetrachloroalkanes and  $\alpha, \beta$ -unsaturated  $\alpha, \alpha, \omega$ -trichloroalkenes we have obtained picrates from the isothiuronium derivatives with structures  $\text{CCl}_3(\text{CH}_2)_n\text{SC}(=\text{NH})\text{NH}_2 \cdot \text{C}_6\text{H}_2(\text{NO}_2)_3\text{OH}$ , where  $n = 4, 6, 8, 10, 12$ , and  $\text{CCl}_2=\text{CH}(\text{CH}_2)_x\text{SC}(=\text{NH})\text{NH}_2 \cdot \text{C}_6\text{H}_2(\text{NO}_2)_3\text{OH}$ , where  $x = 3, 5, 7, 9, 11, 13$ .

2. The synthesis of the corresponding picrates of isothiuronium derivatives can be used for purposes of identification of  $\alpha, \alpha, \alpha, \omega$ -tetrachloroalkanes and  $\alpha, \alpha, \omega$ -trichloroalkenes.

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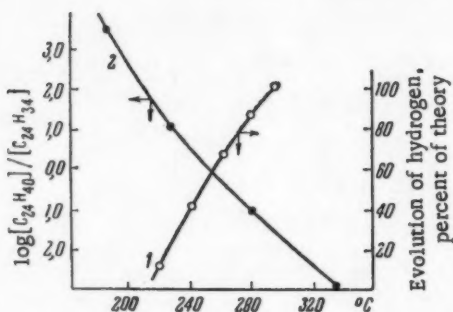
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# SOME PECULIARITIES IN THE LIQUID PHASE DEHYDROGENATION OF BICYCLIC HIGH MOLECULAR WEIGHT HYDROCARBONS

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The well known reaction of catalytic dehydrogenation of hexamethylene hydrocarbons to aromatics has been studied especially in cases of transformation of monocyclic hydrocarbons of comparatively low molecular weight. At the same time there is no less interest in liquid phase catalytic dehydrogenation of high molecular weight hydrocarbons which contain several hexamethylene rings in the molecule. In the present work we have studied the liquid



Degree of dehydrogenation of dicyclohexyldecane and the ratio of phenylcyclohexyldecane and diphenyldecane in the equilibrium mixture at different temperatures (2).

phase dehydrogenation of hydrocarbons with the composition  $C_{24}$  in the temperature range 200-300°. The study was carried out in the apparatus previously described [1], using platinized carbon as the catalyst. From the figure (curve 1) we see the results of amount of hydrogen evolved (in % of theory) for various temperatures in the dehydrogenation of 1,1-dicyclohexyldecane. We cannot strictly call this an equilibrium curve, since for that we need the same results in the hydrogenation of the corresponding aromatic hydrocarbon. This unfortunately could not be carried out, evidently because of the small adsorption of hydrogen by the catalyst at temperatures above 200°. There is reason to assume that the results shown in the figure are close to those of equilibrium conditions, since all the experimental points for the amount of hydrogen evolved obtained in the experiment were determined after many hours holding of the starting hydrocarbon at the corresponding temperature, and the rate of evolution of hydrogen at the end of the experiment was sharply decreased (tenfold compared to the initial value). It is interesting to note that in spite of the difference in molecular weight, number of rings, and phase state under the experimental conditions, the dehydrogenation curve of dicyclohexyldecane in the figure, in general agrees quite well with the equilibrium curve for dehydrogenation of ethylcyclohexane and propylcyclohexane [2].

Now we consider some peculiarities in the dehydrogenation of bicyclic hydrocarbons. In general, in the dehydrogenation of 1,1-dicyclohexyldecane we can expect formation as the final product of the reaction 1,1-diphenyldecane and as the intermediate, 1-phenyl-1-cyclohexyldecane. We reported previously that the study of the intermediate reaction products of dehydrogenation of 1,1-dicyclohexyldecane at 315° (that is, under conditions when the equilibrium is shifted wholly to the side of 1,1-diphenylcyclohexane), which were separated at the moment of 50% conversion, showed the presence of all three hydrocarbons (that is, 1,1-dicyclohexyldecane, 1-phenyl-1-cyclohexyldecane, and 1,1-diphenyldecane) in approximately equal amounts [1]. In the present investigation we have also studied the composition of the reaction products at 50% conversion (based on hydrogen), but at 245°. From the results in the figure it is not difficult to conclude that this percent conversion corresponds to the equilibrium conversion for 245° and thus the reaction products are no longer intermediate, but final. It was shown that in this case the reaction product contains 74% 1-cyclohexyl-1-phenyldecane (I), and, respectively, 13% of 1,1-dicyclohexyldecane (II), and 1,1-diphenyldecane (III). Hence we can conclude that hydrocarbon (I) is thermodynamically more stable than the equimolecular mixture of hydrocarbons (II) and (III). This conclusion was also confirmed by the following experiment: An equimolecular mixture of hydrocarbons (II) and (III) was submitted to analogous conversion at 250°. Evolution of hydrogen did not occur, and study of the reaction products showed again the presence

of all three hydrocarbons in about the same proportions, that is, 74: 13: 13. 1-Phenyl-1-cyclohexyldodecane under these conditions, as expected, changed little, undergoing slight dehydrogenation with formation of diphenyldodecane.

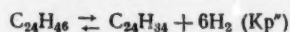
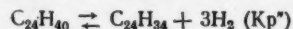
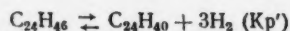
#### Thermodynamic Parameters of the Hydrocarbons Studied

| Hydrocarbon        | $\Delta H^\circ$ ,<br>kcal/M,<br>298,16°K | $S^\circ$ ,<br>kcal/M°<br>298,16°K | $C_p$ ,<br>kcal/M°<br>298,16°K |
|--------------------|---|------------------------------------|--------------------------------|
| $C_{24}H_{46}$ (I) | -129430                                   | 165,62                             | 143,00                         |
| $C_{24}H_{40}$ (I) | -83430                                    | 166,33                             | 146,06                         |
| $C_{24}H_{34}$ (I) | -35110                                    | 163,70                             | 141,93                         |

We carried out separation of the reaction products by chromatography, using as adsorbent silica gel, grade ASK, and as desorbent, n-hexane. The properties of hydrocarbons (II) and (III) obtained in the dehydrogenation corresponded to the properties of the same hydrocarbons synthesized according to the Grignard reaction [3].

The observed characteristics of the dehydrogenation of bicyclic hydrocarbons at temperatures below 300° can recommend this as a preparative method for obtaining some difficultly available hydrocarbons with a mixed structure. Thus, by the contact of 1,3-bis-(2,5-dimethylcyclohexyl)-2-amypropane with platinumized carbon at 250° we have obtained with a 50% yield 1-(2,5-dimethylcyclohexyl)-3-(2,5-dimethylphenyl)-2-amypropane, with  $n_D^{20}$  1.4990. The ratio between phenylcyclohexyldodecane and diphenyldodecane in various mixtures was also determined by calculation on the basis of a study of the thermodynamic properties of the hydrocarbons (I), (II), and (III). In the work [4] data has already been reported on the heat capacity of these hydrocarbons in the temperature range 13-298,16°K, and also data on the heat and temperature of the phase transformation. Further, we also determined experimentally the heat of combustion of the same products. A summary of the thermodynamic data for all three hydrocarbons is given in the table.

Taking for all three hydrocarbons the same temperature relation of heat capacity in the range 298,16-600°K we calculated  $K_p$  for the reaction:



and then the ratio  $C_{24}H_{40}/C_{24}H_{34}$  in the equilibrium mixture at various temperatures. The results of the calculation are given in the figure (curve 2). It is not difficult to see that in the equilibrium mixture the ratio between phenylcyclohexyldodecane and diphenyldodecane in the range 200-300° changes in very wide limits (from 100 to 0.01). At the same time, the experimentally obtained point for 245° (curve 1) corresponds to the ratio

$$\frac{C_{24}H_{40}}{C_{24}H_{34}} = \frac{74}{13} = 5,7$$

which agrees well enough with the calculations from thermodynamic data.

#### SUMMARY

1. We have studied the liquid phase catalytic dehydrogenation of 1,1'-dicyclohexyldodecane and 1,3-bis(2,5-dimethylcyclohexyl)-2-amypropane in the temperature range 200-300°.

2. At 245°, that is, under conditions in which the evolution of hydrogen corresponds to about half the theoretical, the reaction product contains a considerable amount (50-75%) of the hydrocarbon with the mixed structure: 1,1-phenylcyclohexyldodecane and 1-(2,5-dimethylphenyl)-2-amy-3-(2,5-dimethylcyclohexyl)-propane.

3. We have carried out thermodynamic calculations for the equilibrium concentration in the system 1,1-dicyclohexyldodecane  $\rightleftharpoons$  1,1-phenylcyclohexyldodecane  $\rightleftharpoons$  1,1-diphenyldodecane in the temperature range 0-350°.

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# THE MICRODETERMINATION OF PRIMARY AND SECONDARY SATURATED NITROCOMPOUNDS

V. A. Klimova and K. S. Zabrodina

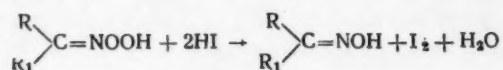
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The suggested micromethod for determination of primary and secondary saturated nitrocompounds is based on the reduction by hydriodic acid of the aci-form of the nitrocompound, as a result of which an oxime is formed and iodine is liberated.



The iodine is titrated with a solution of sodium thiosulfite and thus the content of the nitrogroup is determined. This reaction was used by Moldavskii and Ivanova [1] for the macrodetermination of nitrocyclohexane.

## EXPERIMENTAL

An alcoholic solution of alkali was prepared by dissolving 2 g of potassium hydroxide in 20 ml of water, after which the volume of the solution was brought to 100 ml with 96% ethyl alcohol. In a 150 ml conical flask with a ground glass stopper and containing 3 ml of the 2% alcoholic solution of potassium hydroxide was placed a sample of the compound to be analyzed. After 10 min, 3 ml of a 50% aqueous solution of potassium iodide was added to the flask and the contents were stirred, after which 5 ml of 15% hydrochloric acid was added. The flask was stoppered, the reaction solution was again mixed, and allowed to stand in the dark for 10 min. Then 50 ml of water was added to the flask and the iodine which had been liberated was titrated with 0.01 N sodium thiosulfite solution, adding at the end of the titration as an indicator 2 ml of 0.5% starch solution. The content of nitrogroups was calculated by the formula

$$\% \text{NO}_2 = \frac{23,004 \cdot N (a - b) \cdot 100}{m}$$

where  $N$  is the normality of sodium thiosulfite solution;  $a$  the volume (in milliliters) of the sodium thiosulfite solution needed for titration of the sample;  $b$  the volume of sodium thiosulfite solution used in titration of a control solution;  $m$  the sample weight in milligrams. The results of determination of nitrocompounds are shown in the table.

| Substance        | Sample, mg | ml 0.01 N $\text{Na}_2\text{S}_2\text{O}_3$ used | Content of $\text{NO}_2$ groups, % |       |            |
|------------------|------------|--|------------------------------------|-------|------------|
|                  |            |  | theory                             | found | difference |
| Nitroethane      | 2,144      | 5,692  | 61,29                              | 61,07 | -0,22      |
|                  | 2,253      | 6,004  | 61,29                              | 61,30 | +0,01      |
| 1-Nitropropane   | 2,120      | 4,704  | 51,64                              | 51,04 | -0,60      |
|                  | 2,151      | 4,768  | 51,64                              | 50,99 | -0,65      |
| 2-Nitropropane   | 3,784      | 8,484  | 51,64                              | 51,58 | -0,06      |
|                  | 3,947      | 8,894  | 51,64                              | 51,84 | +0,20      |
| Nitrocyclohexane | 5,010      | 7,696  | 35,62                              | 35,34 | -0,28      |
|                  | 4,969      | 7,652  | 35,62                              | 35,43 | -0,19      |

#### SUMMARY

We have proposed a method for microdetermination of nitrogroups in primary and secondary saturated nitrocompounds based on reduction by hydriodic acid of the aci-form of the nitrocompound to the oxime.

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# TELOMERIZATION OF ETHYLENE AND CARBON TETRACHLORIDE OR CHLOROFORM IN THE PRESENCE OF THE HEXACARBONYLS OF CHROMIUM, MOLYBDENUM, AND TUNGSTEN

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Previously [1] we reported that telomerization of ethylene with carbon tetrachloride, chloroform, and ethyl trichloroacetate could be initiated by small additions of iron pentacarbonyl.\* At the present time we have studied the possibility of using the hexacarbonyls of chromium, molybdenum, and tungsten as initiators of this reaction. Chromium hexacarbonyl is the most effective of the initiators studied; in its presence the reaction between ethylene and carbon tetrachloride or chloroform occurs smoothly at 115-120°, leading to the preparation of  $\alpha, \alpha, \alpha, \omega$ -tetrachloroalkanes and  $\alpha, \alpha, \alpha$ -trichloroalkanes, respectively. Molybdenum and tungsten hexacarbonyls under similar conditions showed less effectiveness, giving not only less conversion, but also forming complex mixtures of side products when the reaction was carried out in their presence. Thus, telomerization of ethylene with carbon tetrachloride and chloroform was initiated by a series of metal carbonyls.

## EXPERIMENTAL

The experiments were carried out in a rocking autoclave of stainless steel, capacity 500 ml. In the autoclave we put carbon tetrachloride or chloroform and 0.1 g of the corresponding hexacarbonyl; air was replaced in the autoclave by nitrogen, after which ethylene was introduced. The reaction mixture was heated for 4-5 hr at 115-120°. The reaction products were separated by fractionation in a vacuum and showed constants agreeing with the literature [3, 4] for these substances. The results are given in the table.

| Carbonyl                 | Telo-<br>gen    | Amt.<br>of<br>telo-<br>gen, g | Change<br>in pres-<br>sure at<br>115-120° | Con-<br>version<br>of telo-<br>gen, % | Isolated individual telomer-homologs<br>$\text{CCl}_3(\text{CH}_2\text{CH}_2)_n \times (x = \text{H, Cl})$ |       |       |       |       |
|--------------------------|-----------------|-------------------------------|---|---------------------------------------|--|-------|-------|-------|-------|
|                          |                 |                               |   |                                       | $n=1$  | $n=2$ | $n=3$ | $n=4$ | $n>4$ |
| $\text{Cr}(\text{CO})_6$ | $\text{CHCl}_3$ | 223                           | 110-75                                    | 27                                    | (7)  | 20    | 12    | 5     | (22)  |
| $\text{Cr}(\text{CO})_6$ | $\text{CCl}_4$  | 240                           | 100-60                                    | 52                                    | (20)   | 84    | 30    | 10    | (15)  |
| $\text{Cr}(\text{CO})_6$ | $\text{CCl}_4$  | 240                           | 35-5                                      | —                                     | 33   | (18)  |       |       |       |
| $\text{Mo}(\text{CO})_6$ | $\text{CCl}_4$  | 240                           | 145-80                                    | 23                                    |  | 13    |       |       |       |
| $\text{W}(\text{CO})_6$  | $\text{CCl}_4$  | 240                           | 110-95                                    | 20                                    | (8)  | 27    | 7     | (6)   |       |

\* Figures without parentheses show weight of individual substances obtained. Figures in parentheses show weight of products obtained as a wide fraction, not further studied.

## SUMMARY

The reaction of telomerization of ethylene with carbon tetrachloride or chloroform is initiated by hexacarbonyls of chromium, molybdenum, and tungsten at 115-120°, forming  $\alpha, \alpha, \alpha, \omega$ -tetrachloroalkanes and  $\alpha, \alpha, \alpha$ -trichloroalkanes, respectively.

\* When our work was already in press we learned that in an English patent [2] the possibility was suggested by using iron pentacarbonyl for initiation of telomerization of ethylene with carbon tetrachloride or chloroform.

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# GASOMETRIC DETERMINATION OF ALKYL RADICALS IN POLYALKYLSILOXANES AND SILICOFUNCTIONAL ORGANIC SILICON COMPOUNDS

M. G. Voronkov and V. T. Shemyatenkova

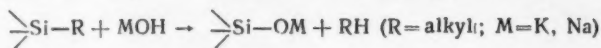
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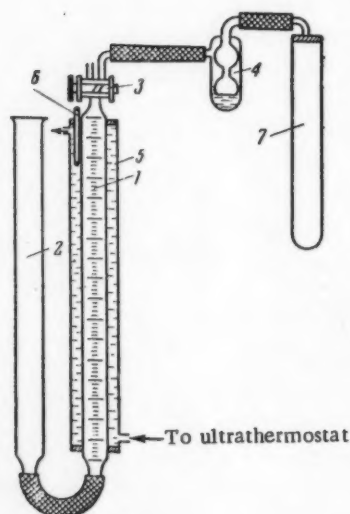
Original article submitted June 18, 1960

Among the various methods for analysis of organic silicon polymers and monomers [1-4] there has so far been no process for quantitative determination of alkyl radicals bound to a silicon atom. It seemed of interest to us to fill this gap, basing our work on the ability of the Si-C bond to be split more or less easily by the action of such powerful nucleophilic reagents as the hydroxides of alkali metals [4-6] according to the scheme:



A detailed study of this reaction permitted us to find the optimum conditions in which splitting of the alkyl radicals from the silicon atom occurred practically completely, with formation of a stoichiometric volume of gaseous hydrocarbon RH from which we could estimate the amount of radical R bound to the silicon atom.

The method of analysis was as follows. The determination was carried out in the apparatus shown in the figure; it consisted of a thermostatically controlled gas buret, 1, connected with an equalizing vessel (buret) filled with an acidified, saturated solution of NaCl or mercury, 2 (Lunge type nitrometer). The three-way stopcock, 3, joined the gas buret through an absorber with concentrated  $\text{H}_2\text{SO}_4$  with the steel tube, 7. In this tube we placed the sample of the substance to be studied (0.1-0.15 g), added 2-3 g of powdered KOH and heated it in a tubular electric furnace. Decomposition occurred at 250-270° and was continued to full stoppage of gas evolution (up to 2 hr). During the decomposition of the sample, the equalizing vessel should be kept above the level of the liquid in the gasometer buret in order to keep in the system a small excess pressure. At the end of gas evolution tube 7 was removed from the oven and cooled to the temperature of the buret. Further readings of the volume of gas were carried out in the usual way for gasometric analysis.



In the table we give the results of determination of content of methyl and ethyl groups in individual oligomeric organosiloxanes and in polymeric compounds of this type. The results show that the method permits determination of methyl and ethyl radicals in compounds of this class with an average accuracy of  $\pm 0.7\%$  (maximum variation  $\pm 1.6\%$ ). Analogous accuracy is attained in determination of the content of radicals in mixtures of polymethyl

and polyethylsiloxanes. The presence of aromatic radicals in the siloxane skeleton does not change the determination. The method can also be used for determination of hydrocarbon radicals in silicofunctional compounds which contain hydrolyzable substituents on the silicon atom, for example, in alkylhalogensilanes. This can be illustrated by the analytical data on methylphenyldichlorosilane: found:  $\text{CH}_3$  7.67, 8.54%; calculated:  $\text{CH}_3$  7.87%.

We must note that the splitting of alkyl radicals from silicon atoms not also connected with oxygen atoms or with functional groups which raise the electrophilic character of the central silicon atom is not complete. Therefore the method of splitting by alkali under these conditions for analysis of silicohydrocarbons is not usable. A study of the composition of gas from the splitting of polymethylsiloxanes by KOH showed that it was not always pure

methane, as the literature indicates [5, 6]. In a number of cases the gas contained along with methane, ethane, and also traces of hydrogen and ethylene. However, the volume of these mixtures in all cases was practically stoichiometrically the same as the content of methyl radicals in the siloxane studied (the variation usually did not exceed 2 absolute %).

Results of Gasometric Determination of Alkyl Radicals R (R=CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>) in Polyalkylsiloxanes

| Polyalkylsiloxane  | Content of R, % |       | Difference, absolute, % |
|--|-----------------|-------|-------------------------|
|  | found           | calc. |                         |
| [(CH <sub>3</sub> ) <sub>2</sub> SiO] <sub>3</sub>   | 41,8            | 40,5  | +1,3                    |
| [(CH <sub>3</sub> ) <sub>2</sub> SiO] <sub>4</sub>   | 39,3            | 40,5  | -1,2                    |
| [(CH <sub>3</sub> ) <sub>2</sub> SiO] <sub>3000</sub>  | 40,4            | 40,5  | -0,1                    |
| [(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> SiO] <sub>3</sub>   | 57,6            | 56,9  | +0,7                    |
| [(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> SiO] <sub>4</sub>   | 57,2            | 56,9  | +0,3                    |
| [CH <sub>3</sub> (C <sub>6</sub> H <sub>5</sub> )SiO] <sub>n</sub>   | 11,6            | 11,0  | +0,6                    |
| (CH <sub>3</sub> ) <sub>3</sub> SiOSi(C <sub>6</sub> H <sub>5</sub> )CH <sub>3</sub> [OSi(CH <sub>3</sub> ) <sub>2</sub> CH <sub>3</sub>   | 34,6            | 36,2  | -1,6                    |
| (CH <sub>3</sub> ) <sub>3</sub> Si[OSi(C <sub>6</sub> H <sub>5</sub> )CH <sub>3</sub> ] <sub>2</sub> OSi(CH <sub>3</sub> ) <sub>3</sub>  | 26,5            | 27,4  | -0,9                    |
| (CH <sub>3</sub> ) <sub>3</sub> Si[OSi(C <sub>6</sub> H <sub>5</sub> )CH <sub>3</sub> ] <sub>12</sub> OSi(CH <sub>3</sub> ) <sub>3</sub>   | 15,1            | 14,8  | +0,3                    |
| (CH <sub>3</sub> ) <sub>3</sub> SiOSi(CH <sub>3</sub> ) <sub>2</sub> [OSi(C <sub>6</sub> H <sub>5</sub> )CH <sub>3</sub> ] <sub>2</sub> OSi(CH <sub>3</sub> ) <sub>3</sub>                   | 24,5            | 25,6  | -1,1                    |
| (CH <sub>3</sub> ) <sub>3</sub> Si[OSi(CH <sub>3</sub> ) <sub>2</sub> ] <sub>20</sub> [OSi(C <sub>6</sub> H <sub>5</sub> )CH <sub>3</sub> ] <sub>14</sub> OSi(CH <sub>3</sub> ) <sub>3</sub> | 24,9            | 24,4  | +0,5                    |
| (CH <sub>3</sub> ) <sub>3</sub> Si[OSi(C <sub>6</sub> H <sub>4</sub> F)CH <sub>3</sub> ] <sub>10</sub> OSi(CH <sub>3</sub> ) <sub>3</sub>  | 15,0            | 14,8  | +0,2                    |
| [CH <sub>3</sub> SiO <sub>1,5</sub> ] <sub>2</sub>   | 24,0            | 22,4  | +1,6                    |
| [4C <sub>6</sub> H <sub>5</sub> SiO <sub>1,5</sub> ·CH <sub>3</sub> (C <sub>6</sub> H <sub>5</sub> )SiO] <sub>n</sub>  | 2,3             | 3,0   | +0,7                    |
| H[OSi(ONa)CH <sub>3</sub> ] <sub>12</sub> OH   | 17,1            | 15,1  | +2,0                    |

\* Average of several determinations.

A. A. Khvoshchevskaya, L. M. Kharchevnikova, and Z. I. Shabarova took part in the experimental portion of this work.

# SUMMARY

We have worked out a gasometric method for determination of alkyl radicals (CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>) in polyorganosiloxanes and silicofunctional organic silicon compounds, based on their splitting as the corresponding hydrocarbons (CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>) by alkali. The accuracy of the method is 1-2%.

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# THE METASTABLE EQUILIBRIUM IN THE SYSTEM

## $\text{CaCO}_3\text{--MgCO}_3\text{--H}_2\text{O}$

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The reaction of calcium and magnesium carbonates in a water medium is related to the processes of solution and reciprocal salting out, supersaturation, complex formation in solution, formation of chemical compounds, etc. To study these effects in the system  $\text{CaCO}_3\text{--MgCO}_3\text{--H}_2\text{O}$  over a wide temperature interval is the problem of this investigation. For the study we used the metastable forms of the carbonates which we synthesized: Aragonite ( $\text{CaCO}_3$ ) and nesquehonite ( $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$ ). The solubility was studied at 0, 20, 40, 55, 70, and 90° and  $P_{\text{CO}_2}$  about 1 atm. The solutions were analyzed for their content of  $\text{HCO}_3^-$ ,  $\text{Ca}^{++}$ , and  $\text{Mg}^{++}$ , and their density was also determined. Similar control analyses for  $\text{HCO}_3^-$  were run periodically for 1-2 days and served to show the establishment of equilibrium. The solid phase was studied chemically and microscopically. First we studied the solubility in water of pure magnesium carbonate at 0-90° and  $P_{\text{CO}_2}$  about 1 atm.

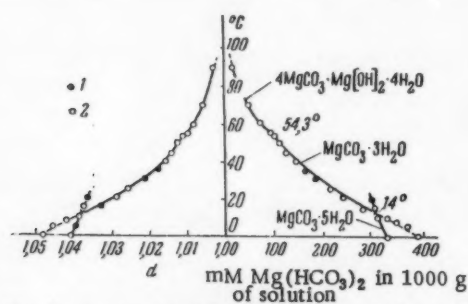


Fig. 1. System  $\text{MgCO}_3\text{--H}_2\text{O}$  at  $P_{\text{CO}_2}$  about 1 atm. 1) Literature values [1]; 2) our results.

in the system  $\text{MgCO}_3\text{--H}_2\text{O}$  is preserved under definite conditions and in the presence of calcium carbonate. The solubility in the ternary system  $\text{CaCO}_3\text{--MgCO}_3\text{--H}_2\text{O}$  was studied by the usual method, by adding definite portions of  $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$  to a solution saturated with aragonite (with an excess of crystals at the bottom of the vessel), and then stirring the mixture intensively until equilibrium was reached.

When we introduced into the solution slowly and in portions the same amounts of  $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$ , we obtained at 0°, as distinguished from the other isotherms, a second solubility curve, indicated in Fig. 2 by dotted lines; here in the solid phase (in the eutonic) there is always crystallization of magnesium carbonate trihydrate along with aragonite. Long stirring of the mixture (sometime: up to 10 days) did not help replacement of aragonite by calcite, shifting from the dotted curve to the solid (Fig. 2). All the solubility isotherms except the dotted curve were of the same type, concave to the ordinate; this shows that calcium carbonate is strongly displaced from the solution by magnesium carbonate at all temperatures; thus, at 0° its solubility falls from 15.40 in pure water to 0.55 mM per 1000 g of solution when it is in equilibrium with the second phase, magnesium carbonate pentahydrate and aragonite (point a, Fig. 2). However, the content of calcium in the eutonic solution is increased fivefold by its saturation with magnesium carbonate trihydrate instead of pentahydrate (point b, Fig. 2); the composition of the liquid phase at point a is 330.4 mM  $\text{Mg}(\text{HCO}_3)_2$  and 0.55 mM  $\text{Ca}(\text{HCO}_3)_2$ , and at point b is 396.0 and 2.78 mM per 1000 g of solution, respectively. In other words, the less hydrated but more soluble at 0° magnesium carbonate  $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$  salts

The results of the investigation are given in Figs. 1 and 2. The solubility curve of Fig. 1 has three branches corresponding to crystallization of the basic salt  $4\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$ , the trihydrate,  $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$ , and the pentahydrate  $\text{MgCO}_3 \cdot 5\text{H}_2\text{O}$ . The curve of density of the solutions fully repeats the course of the solubility curve (Fig. 1). The transition of the pentahydrate from a magnesium carbonate into the trihydrate and the latter into the basic salt occurred at temperatures of about 14 and 54.3°, respectively. However, the pentahydrate could exist in the system even at higher temperatures (to 20° and perhaps higher; see dotted line, Fig. 1) and the trihydrate at lower temperatures; the solubility of the latter then increased, reaching at 0° 397.6 mM  $\text{Mg}(\text{HCO}_3)_2$  in 1000 g of solution, against 339.2 mM for the pentahydrate. Such behavior of the hydrated forms of magnesium carbo-

calcium carbonate out of solution less than  $\text{MgCO}_3 \cdot 5\text{H}_2\text{O}$  at the same temperature. Obtaining two solubility curves for  $0^\circ$  suggests that an analogous picture may also be found in the system at other temperatures at which  $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$  exists in the labile state ( $14^\circ$  and below; see dotted line, Fig. 1). This shows that calcium carbonate at the same time and under definite conditions may be "held" in considerable quantity in strong solutions of magnesium salts, that is, under conditions of slow enrichment of the latter. Under these conditions we do not find increase in reciprocal solubility of the carbonates because of complex formation, as is shown by the course of all the isotherms of the diagram (Fig. 2). The absence of complex formation in the system  $\text{CaCO}_3\text{--MgCO}_3\text{--H}_2\text{O}$  at  $28.4^\circ$  and  $P_{\text{CO}_2}$  about 1 atm is also shown on the basis of data of measurement of pH in the solution by Halla and Tassel [2]. Greenwald and co-workers [3] described the formation in solution of a complex ion of  $\text{CaHCO}_3^+$  and  $\text{MgHCO}_3^+$  in the presence of  $\text{KHCO}_3$  and at low  $P_{\text{CO}_2}$ , that is, under different conditions. We have shown that the solubility of salts in the system  $\text{CaCO}_3\text{--MgCO}_3\text{--H}_2\text{O}$  can sometimes be changed under isothermal conditions and depends on the nature of the magnesium carbonate which saturates the solution. The resulting equilibrium diagram (Fig. 2) is of metastable type; it differs from the diagram of a stable type [4] by the absence of a region of two compounds (dolomite) and is characterized by the presence of regions of crystallization of four metastable phases: aragonite, basic salt, magnesium carbonate trihydrate, and pentahydrate. The results of this study, besides their theoretical interest, have practical value for the treatment of carbonate minerals and natural brines which are rich in magnesium salts into heat insulating materials of the type of newel and sovelite.

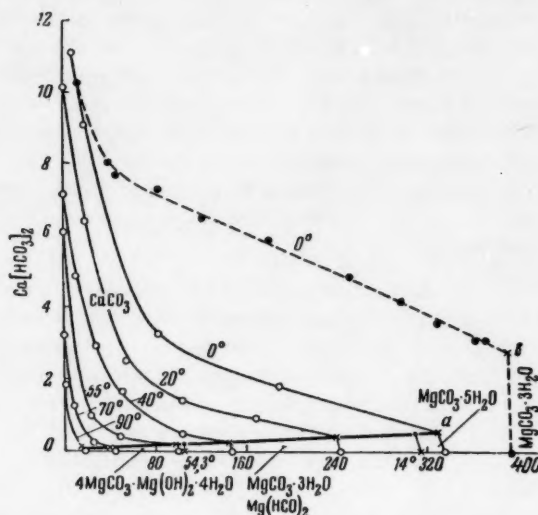


Fig. 2. System  $\text{CaCO}_3\text{--MgCO}_3\text{--H}_2\text{O}$  at  $P_{\text{CO}_2}$  about 1 atm; concentration of  $\text{Ca}(\text{HCO}_3)_2$  and  $\text{Mg}(\text{HCO}_3)_2$  expressed in millimoles per 1000 g solution (diagram of metastable equilibrium type).

#### SUMMARY

1. We have studied the solubility of the metastable phases in the system  $\text{CaCO}_3\text{--MgCO}_3\text{--H}_2\text{O}$  at  $0\text{--}90^\circ$  and  $P_{\text{CO}_2}$  about 1 atm and shown the absence of complex formation in solution, and the presence of a marked salting out of calcium carbonate by magnesium salts; the salting out action of the latter depends on temperature, nature of the solid phase which saturates the solution, and other factors.

2. The results of the investigation are of practical value for the technology of obtaining heat insulating materials of the type of newel and sovelite based on carbonate minerals and brines rich in magnesium salts.

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THE EFFECT OF CONFIGURATION OF NITRODIENOPHILES  
 $R-CH=CH-NO_2$  ON THEIR CONDENSATION  
WITH CYCLOPENTADIENE

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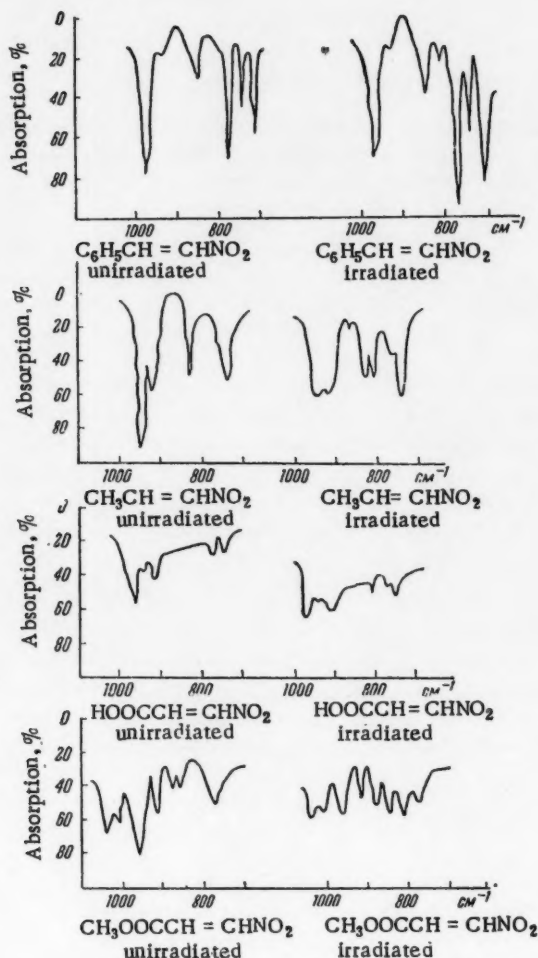
In one of their papers, Tamelen and Thiede [1] showed chemically that the methyl and nitro groups in 1-nitro-1-propylene are in the trans-position to each other. We decided to show the spatial arrangement of the substituents in 1,2-disubstituted ethylenes of the type  $NO_2CH=CHR$  and to study the effect of such dienophiles on their reaction with cyclopentadiene. As the 1,2-disubstituted ethylenes we chose 1-nitro-1-propylene,  $\beta$ -nitrostyrene,  $\beta$ -nitroacrylic acid, and its methyl ester. We took the infrared absorption spectra of 1-nitro-1-propylene,  $\beta$ -nitrostyrene,  $\beta$ -nitroacrylic acid, and its methyl ester on a UR-10 spectrometer. 1-Nitro-1-propylene, which was a liquid, was taken as such, and the other three nitroolefins in the solid state, by depositing their methylene chloride solutions on a KBr "glass" and evaporating the solvent. In the spectra of all the compounds studied we found bands in the region  $945-970\text{ cm}^{-1}$  (see the figure) which we assigned to nonplanar deformation oscillation of hydrogen atoms, shown only in a trans-configuration of the molecule [2-4].

In order to show more strictly the trans-arrangement of the substituents in the nitroolefins considered, and to show the effect of the spatial arrangement of the substituents on the diene condensation, we decided to prepare the same nitroolefins with the cis-arrangement of the substituents and to carry out condensation of the cis- and trans-forms of  $RCH=CHNO_2$  with cyclopentadiene under comparable conditions. We used the results of Kochetkov and co-workers [5] showing that when trans- $\beta$ -chlorovinyl ketone was irradiated with ultraviolet light, it isomerized into cis- $\beta$ -chlorovinyl ketone, and irradiated our olefins with ultraviolet light. All four nitroolefins in methylene chloride solution were irradiated with ultraviolet light for 70 hr, after which their infrared absorption spectra were again taken. We showed that the intensity of the bands in the region  $945-970\text{ cm}^{-1}$  had weakened markedly, and a band appeared in the region  $805\text{ cm}^{-1}$  (see the figure). It is interesting to note that if we take the infrared absorption spectra some time after irradiation, the band in the region  $805\text{ cm}^{-1}$  disappears, and the intensity of the bands  $945-970\text{ cm}^{-1}$  has returned to the former level. For a study of the reverse isomerization with time we took the infrared spectra of the irradiated samples 2 hr, 12 hr, and two days after irradiation. On analysis of the spectra taken 2 hr after irradiation we found an intense band in the region of  $805\text{ cm}^{-1}$  and a much less intense band in the region  $945-970\text{ cm}^{-1}$  than in the starting forms. After 12 hr the intensity of the first band had markedly lessened and the intensity of the second had almost reached the intensity of the unirradiated form. After two days the spectra of the irradiated samples were entirely identical with those of the unirradiated substances. It is probable that the case of the reverse isomerization is the reason that we could not obtain pure cis-isomers (we could not attain full disappearance of the bands in the region  $945-970\text{ cm}^{-1}$ ).

Thus, the appearance of bands in the region  $805\text{ cm}^{-1}$  on irradiation, and the disappearance of these bands with holding of the irradiated samples can be due to isomerization of the trans-forms of the nitroolefins into the cis-forms on irradiation, and the reverse isomerization of the cis- to the trans-forms on holding.

For comparison of the reactivity of the cis- and trans-forms of the nitroolefins  $RCH=CHNO_2$  in the Diels-Alder reaction we carried out condensation of irradiated and unirradiated  $\beta$ -nitrostyrene with cyclopentadiene. Trans- $\beta$ -styrene with m. p.  $57^\circ$  was irradiated with ultraviolet light for 70 hr and we obtained cis- $\beta$ -nitrostyrene as an oil with an admixture of some quantity of crystals of trans- $\beta$ -styrene. The liquid cis- $\beta$ -styrene even at room temperature reacted with cyclopentadiene with slight evolution of heat. To a solution of 1.13 g (0.008 M) of

$\beta$ -nitrostyrene irradiated with ultraviolet light for 70 hr and a small amount of pyrogallol in 4 ml of dry benzene we added with stirring 0.52 g (0.008 M) of freshly distilled cyclopentadiene. The temperature of the mixture then rose from 22° to 24.5°. The flask was tightly stoppered and left standing for two days. After distillation of unreacted starting substances, the residue was distilled. We obtained 0.95 g (62%) of 2-nitro-4-phenylbicyclo-(2,2,1)-5-heptene with b. p. 149.5° (2 mm);  $n_D^{20}$  1.5700. Unirradiated *trans*- $\beta$ -nitrostyrene did not react with cyclopentadiene under the same conditions and was recovered unchanged.



#### SUMMARY

1. The infrared absorption spectra of 1-nitro-1-propylene,  $\beta$ -nitrostyrene,  $\beta$ -nitroacrylic acid, and its methyl ester confirm the *trans*-structure of the 1,2-disubstituted nitroolefins  $RCH=CHNO_2$ .
2. On irradiation by ultraviolet light the *trans*-nitroolefins  $RCH=CHNO_2$  isomerize into the corresponding *cis*-nitroolefins.
3. In the case of  $\beta$ -nitrostyrene and cyclopentadiene it has been shown that the spacial arrangement of the substituents in the nitroolefins  $RCH=CHNO_2$  has a considerable effect on the occurrence of the diene synthesis.

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## THE DETERMINATION OF MICROGRAM QUANTITIES OF AMINO ACIDS IN NATURAL WATERS

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The determination of the amino acid content in natural waters and the related study of the distribution and processes of transformation of amino acids and proteins in reservoirs, the state of proteins dissolved in water, etc., has encountered serious difficulties of a methodological nature. Besides the very low content of amino acids, the difficulties depend on the presence in the water of a much greater quantity of mineral and colored organic substances which interfere with the determination. In special cases the difficulty of determination of amino acids in the hydrolyzates of organic substances in natural waters can be overcome by use of semimicro methods [1]. However, such methods, which require several tenths of a liter for a determination cannot be widely used in hydrochemical investigations.

In the present paper we suggest a method which permits determination of the amino acids in a comparatively small volume of water containing colored organic (humins) substances. The method is based on the reaction of amino acids with ninhydrin (triketohydrindine) as a result of which blue-violet colored compounds are formed, diketohydrindylidenediketohydrinamines. In spite of the relatively great sensitivity of this reaction it cannot be used in the determination of amino acids in natural waters directly, without their preliminary concentration. For determination of the optimum conditions for concentration of amino acids and choice of sufficiently effective adsorbents, we studied the relation of degree of adsorption of amino acids labeled on the carbon ( $\text{NH}_2\text{CH}_2\text{C}^{14}\text{OOH}$ ) to the pH of solution on several ionites [cationite KU-1, KU-2, KU-6, KF-1, KB-4,  $\text{Al}_2\text{O}_3$  in acid (HCl) form; anionites AN-22,  $\text{Al}_2\text{O}_3$  in alkaline (NaOH) form]. The most effective of these ionites were the strongly acid cationites containing sulfo groups (KU-1 and especially KU-2 and KU-6); the degree of adsorption was clearly related to the pH of the solution; nearly zero at pH 1, it rose quite sharply with increasing pH and reached a maximum at pH 5-9, then decreased. At pH 12 the degree of adsorption was again close to zero. Such a dependence permits us to choose conditions both for concentrating and eluting the amino acids held on the cationite. Concentration was carried out on cationite KU-2 in a neutral solution and then removal was carried out with 2 N ammonia, the excess of which was removed by evaporation of the concentrate on a water bath. The amino acids were determined in the sample prepared in this way. Since the method of carrying out the ninhydrin reaction used in paper chromatography [2-5] was not very suitable for the determination of amino acids in natural waters (the colored organic substances which were soluble in water masked the color of the spots on the paper), we tried to carry out the reaction directly in the solution. Best results were obtained by running it in a mixture of water solution of amino acids with n- or iso-butyl alcohol and a relatively great excess of ninhydrin in the presence of cadmium ions.\* In this case the red colored cadmium complex evidently even at the moment of formation enters the alcohol layer, which prevents its rapid destruction by excess ninhydrin, as occurs in carrying out the reaction in water solution. If the reaction is run in neutral solution, the colored organic substances (humins) which are dissolved in the natural water remain almost entirely in the water layer and so do not interfere with the determination. The cadmium complex is easily decomposed by citrates or tartrates. Then the red color of the alcohol solution changes to blue-violet, a more suitable color for photometry. The minimum amount of amino acid content determined by photometric measurement of the optical density of the solution is 2-2.5  $\mu\text{g}$  calculated on the amino nitrogen. The linear dependence of excitation of the alcohol solution on amino acid concentration is kept within the limits 2-30  $\mu\text{g}$  N in the sample (volume of alcohol solution 6 ml, cuvette, 10 mm).

\* As was shown, the ions of some heavy metals, especially cadmium, bind the product of reaction of amino acids with ninhydrin in a complex which assures more even development of the color of the solution.

The procedure is as follows: 1 liter of the water to be studied is passed through a chromatographic column (1 x 20 cm) with cationite KU-2 in the H form at a rate of 10-12 drops per minute. Then the amino acids are removed with 80 ml of 2 N solution of ammonia, the eluate is evaporated in a small porcelain dish to dryness on a water bath, and the dry residue is washed out with 2 ml of distilled water into a 50 ml flask with a ground glass stopper, and 1 ml of ninhydrin reagent is added (75 mg CdCl<sub>2</sub>, 6 ml of water, 0.3 ml of glacial acetic acid, and 2 g of ninhydrin in 100 ml of acetone) [6], along with 2 drops of saturated

cadmium chloride solution and 5 ml of butyl alcohol. The glass stopper of the flask is fastened with a rubber ring and the flask is placed for exactly 15 min in a boiling water bath. After cooling, the mixture is transferred to a calibrated flask with a 1 ml solution of Rochelle salt (25 g/100 g of water), the alcohol layer is brought to 6 ml and the contents of the flask are shaken (here the cadmium complex is decomposed and the red color of the alcohol solution changes to blue-violet) and then centrifuged. Five ml is removed from the alcohol layer and 0.3 ml of butyl alcohol is added (to break up the fine water emulsion in the alcohol solution), and the solution is submitted to photometry on the photoelectric colorimeter with a red light filter. The amino acid content is determined from a calibration curve constructed with a standard solution of glycine treated in an analogous way. The method was checked by determination of amino acids in samples of natural water with the addition of known amounts of glycine (see the table).

Results of Determination of Amino Acids in Samples of Natural Water with Addition of Known Amounts of Glycine

| Sample studied                      | $\mu\text{g N/liter}$ |      |
|-------------------------------------|-----------------------|------|
|                                     | found                 | calc |
| River Don Water (Nov.)              | 8                     |      |
| The same                            | 8                     |      |
| The same + 14 $\mu\text{g N/liter}$ | 20                    | 22   |
| " " + 21 $\mu\text{g N/liter}$      | 27                    | 29   |
| " " + 21 $\mu\text{g N/liter}$      | 28                    | 29   |
| River Don Water (June)              | 6                     |      |
| The same + 7 $\mu\text{g N/liter}$  | 13                    | 13   |
| " " + 14 $\mu\text{g N/liter}$      | 17                    | 20   |
| Water of the Tsimlianskii reservoir | 4                     |      |
| The same + 7 $\mu\text{g N/liter}$  | 11                    | 11   |

In the spectrophotometric determination we can measure the optical density of the alcohol solution of the cadmium complex directly (at  $\lambda = 505 \text{ m}\mu$ ). Determination of the minimum amino acid content in this case can occur with 1-1.5  $\mu\text{g}$  of amino nitrogen in the sample (measurement carried out on an SF-4 spectrophotometer). For determination of free amino acids in natural water by this method 1 liter of water is sufficient.

#### SUMMARY

1. With a strongly acid cationite KU-2 or KU-6 we can concentrate the amino acids dissolved in natural waters with simultaneous separation of these from the mineral components of the water.
2. We have determined the conditions which permit determination of the amino acids in 1 liter of sample of natural water which contains colored organic substances (humins).

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# THE SYNTHESIS OF DIBENZYLPEPTIDES THROUGH THE p-NITROPHENYL ESTERS OF DIBENZYLAMINO ACIDS

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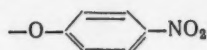
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p-Nitrophenyl esters have found wide use in the synthesis of peptides. A suitable example is the synthesis of the natural hormone oxytocin, in which all eight peptide bonds were formed with the help of p-nitrophenyl esters [1]. The p-nitrophenyl esters of N,N-dibenzyl- $\alpha$ -amino acids, besides their possible use for the synthesis of peptides, also interested us as regards their resistance to splitting. It was shown previously that N,N-dibenzyl- $\alpha$ -amino acid chlorides were completely split, even at room temperature, in their formation. The ease of occurrence of this reaction was explained by the simultaneous action of two benzyl groups which supplied electrons and the chlorine atom which attracted electrons [2]. The group



is a weaker electrophilic substituent and it may be expected that p-nitrophenyl esters of dibenzylamino acids would be more stable.

p-Nitrophenyl esters of N,N-dibenzyl- $\alpha$ -amino acids were synthesized by the method of mixed anhydrides with the ethyl ester of chlorocarbonic acid. We were able to find the simplest method for isolating the p-nitrophenyl esters of dibenzylalanine and dibenzylphenylalanine in analytically pure form with yields of 52-58%. For the reaction we used both the dibenzylamino acids themselves and their salts with HBr. There was no effect on the yield from excess p-nitrophenol with  $N(C_2H_5)_3$  or the temperature of formation of the mixed anhydride and the reaction with it. With dibenzylalanine we could carry out the reaction at room temperature with a yield of 55%. This ester did not dissolve in 30%  $CH_3COOH$  and so in electrophoresis it remained at the line of deposition. We used this property for a study of the thermal stability of the ester. If splitting occurred by a mechanism analogous to the mechanism of splitting of dibenzylamino acid chlorides, we would expect the appearance in electrophoresis in 30%  $CH_3COOH$  of spots of dibenzylamine and disappearance of the spot of the p-nitrophenyl ester. Even after boiling for many hours of the p-nitrophenyl ester of dibenzylphenylalanine in toluene (110°) there was no formation of dibenzylamine; on the contrary, the starting ester appeared at the line of deposition.

We used the esters which we obtained for synthesis of peptides; as the second component we used amino acids with free  $\alpha$ -COOH groups in the presence of  $N(C_2H_5)_3$ . We obtained two dipeptides: Dibenzyl-D,L-phenylalanyl-D,L-proline (yield 73%; m. p. 157.7-158.5°) and the  $\gamma$ -ethyl ester of dibenzyl-D,L-alanyl-L-glutamic acid (isolated as the hydrochloride; yield 87%; m. p. 173-174°). Although a stream of HCl was passed into the solution of the first dipeptide, its hydrochloride was not obtained at all; it was evidently hydrolyzed when the substance was washed with water as shown by the absence of halogen by Beilstein test and by analysis.

## EXPERIMENTAL

p-Nitrophenyl ester of dibenzylalanine. To 2.22 g (0.00827 M) of dibenzylalanine solution in 25 ml of chloroform was added 1.2 ml of  $N(C_2H_5)_3$ . To the solution of -10° was added 0.81 ml of  $ClCO_2C_2H_5$  and the solution was kept at 0° for a half hour and then to it was added a solution of 1.15 g (0.00827 M) of p-nitrophenol and 1.25 ml of  $N(C_2H_5)_3$  in 30 ml of chloroform; the mixture stood overnight at room temperature and then was heated for several minutes to boiling, and the solvent was carefully evaporated off in vacuum to dryness. To the residue was added 20-25 ml of methanol. At first everything dissolved, then as the mixture was stirred, a crystalline precipitate began to come down; after 10-20 minutes it was filtered off and quickly washed with small portions of methanol; yield 1.8 g

(56%). In an analogous way from dibenzylalanine hydrobromide we obtained the p-nitrophenyl ester of dibenzylalanine; yield 59%. For analysis the substance was kept under methanol at room temperature for 2-3 hr, then was filtered and dried in a Fisher apparatus; m. p. 80-82°. Found: C 70.96, 71.10; H 5.70, 5.73; N 7.07, 7.01%.  $C_{23}H_{22}O_4N_2$ . Calculated: C 70.77; H 5.64; N 7.17%. The substance was soluble in ether, benzene, and chloroform.

Synthesis at room temperature. We dissolved 1.4 g (0.005 M) of dibenzylalanine and 0.69 ml of  $N(C_2H_5)_3$  in 15-20 ml of chloroform, and to the solution added 0.48 ml of  $ClCO_2C_2H_5$ ; since the solution then grew warm, the flask was placed for several hours in a water bath at 15-20°. Two to three minutes after adding  $ClCO_2C_2H_5$  we introduced 0.69 g of p-nitrophenol and added 0.69 ml of  $N(C_2H_5)_3$ . At the end of marked gas evolution (after 1 hr) the solution was heated for several minutes to 50-60° and carefully evaporated dry; yield 1.08 g (55%).

$\gamma$ -Ethyl ester of dibenzyl-D,L-alanyl-L-glutamic acid hydrochloride. Two g (0.005 M) of p-nitrophenyl ester of dibenzylalanine was dissolved in 20 ml of chloroform and the solution was treated with 1.2 g (0.0057 M)  $\gamma$ -ethyl ester of glutamic acid hydrochloride and 2.0 ml of  $N(C_2H_5)_3$ . The mixture stood for 20 hr at room temperature, then was boiled for 1.5 hr, filtered, evaporated dry in a vacuum, and the residue was treated with 150 ml of ether; the ether extract was filtered and a stream of HCl was passed into it; a semicrystalline oil precipitated and stood at room temperature for 3-4 days; it was filtered and washed with ether; yield 2 g. For analysis the substance was dissolved in water (it dissolved in the course of 3 hr), filtered from insoluble dipeptide,  $NH_4OH$  was added to an alkaline reactions, and then at once dilute  $CH_3COOH$  was added. The oil which precipitated was extracted with chloroform; the chloroform was evaporated in a vacuum, the residue was dissolved in ether; a stream of HCl was passed through the ether; the precipitate was filtered and dried in a vacuum desiccator over NaOH; m. p. 173-174°. Found: C 62.22, 61.70; H 7.17, 6.88; N 5.79, 6.02%.  $C_{24}H_{31}O_5N_2Cl$ . Calculated: C 62.25; H 6.72; N 6.19%.

#### Synthesis with Dibenzylphenylalanine

In our earlier method for the synthesis of dibenzyl-DL-phenylalanine [3] we erroneously reported the amount of glacial  $CH_3COOH$  saturated with HBr used for hydrobrominolysis of the benzyl ester. In this case, 30 g of the hydrobromide of the benzyl ester of dibenzylphenylalanine was treated with 200 mg of glacial  $CH_3COOH$  saturated with HBr for 7 days at room temperature.

p-Nitrophenyl ester of dibenzylphenylalanine. The substance was obtained in an analogous way to the dibenzylalanine ester (with cooling) from dibenzylphenylalanine itself and from its hydrobromide. Yield 52-58%. Found: C 74.87, 74.81; H 5.79, 5.78; N 6.02, 5.92%.  $C_{29}H_{26}O_4N_2$ . Calculated: C 74.68; H 5.58; N 6.02%. M. p. 94-95°.

Dibenzyl-D,L-phenylalanyl-D,L-proline. A mixture of 4.66 g (0.01 M) of p-nitrophenyl ester of dibenzylphenylalanine, 1.02 g (0.01 M) of proline, and 2.76 g (0.02 M) of  $N(C_2H_5)_3$  was boiled in 40 ml of chloroform for 1.5 hr. The proline dissolved 20 min after the beginning of the reaction. After cooling, the solution was saturated with dry HCl and evaporated dry. The residue was crystallized under ether, filtered, washed several times carefully with ether, then treated with water, and after 1-2 hr was filtered. Washing with water was repeated several times. Yield 3.2 g (73%).

For analysis the substance was reprecipitated from methanol by water. Yield of pure substance 63%; m. p. 157.5-158.5°. Found: C 75.91, 76.18; H 6.92, 6.71; N 6.58, 6.58%.  $C_{28}H_{30}O_3N_2$ . Calculated: C 76.02; H 6.80; N 6.35%.

The substance was hydrolyzed in 20% HCl for several hours. Paper chromatography and electrophoresis gave dibenzylphenylalanine and proline.

#### SUMMARY

1. We have synthesized for the first time the p-nitrophenyl esters of dibenzylalanine and dibenzylphenylalanine, and also the  $\gamma$ -ethyl ester of dibenzyl-D,L-alanyl-L-glutamic acid as its hydrochloride, and dibenzyl-D,L-phenylalanyl-D,L-proline.

2. We have shown the thermal stability of the p-nitrophenyl ester of dibenzylphenylalanine.

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| ABBREVIATION                  | RUSSIAN TITLE                                    | TITLE OF TRANSLATION   | PUBLISHER                                     | Vol.    | Issue | Year      | TRANSLATION BEGAN |
|-------------------------------|--|--|---|---------|-------|-----------|-------------------|
| AE                            | Atomnaya énergiya                                | Soviet Journal of Atomic Energy  | Consultants Bureau                            | 1       | 1     | 1956      |                   |
| Akust. zh.                    | Akusticheskii zhurnal                            | Soviet Physics - Acoustics   | American Institute of Physics                 | 1       | 1     | 1956      |                   |
| Astr.(on). zh(urn).           | Antibiotiki                                      | Antibiotics  | Consultants Bureau                            | 4       | 1     | 1959      |                   |
| Avto(mat), sverka             | Astronomicheskii zhurnal                         | Soviet Astronomy-AJ  | American Institute of Physics                 | 34      | 1     | 1957      |                   |
|                               | Avtomaticheskaya svarka                          | Automatic Welding  | British Welding Research Association (London) |         |       |           |                   |
|                               | Avtomatika i Telemekhanika                       | Automation and Remote Control  | Instruments Society of America                | 27      | 1     | 1959      |                   |
|                               | Biofizika  | Biophysics   | National Institutes of Health*                | 21      | 1     | 1956      |                   |
|                               | Biofizika  | Biochemistry   | Consultants Bureau                            | 41      | 1     | 1959      |                   |
|                               | Byulleten' ékspériméntal'noi biologi i meditsiny | Bulletin of Experimental Biology and Medicine  |   |         |       |           |                   |
|                               | DAN (SSSR)                                       | The translation of this journal is published in sections, as follows:  |   |         |       |           |                   |
|                               | Doklady Akademii Nauk SSSR                       | Doklady Biochemistry Section (Includes: Anatomy, biophysics, endocrinology, evolutionary morphology, genetics, histology, hydrobiology, microbiology, morphology, parasitology, physiology, zoology sections)  | American Institute of Biological Sciences     | 106     | 1     | 1956      |                   |
|                               |  | Doklady Botanical Sciences Sections (Includes: Botany, phytopathology, plant anatomy, plant ecology, plant embryology, plant physiology, plant morphology sections)  | American Institute of Biological Sciences     | 112     | 1     | 1957      |                   |
|                               |  | Proceedings of the Academy of Sciences of the USSR, Section: Chemical Technology   | Consultants Bureau                            | 106     | 1     | 1956      |                   |
|                               |  | Proceedings of the Academy of Sciences of the USSR, Section: Chemistry   | Consultants Bureau                            | 106     | 1     | 1956      |                   |
|                               |  | Proceedings of the Academy of Sciences of the USSR, Section: Physical Chemistry  | Consultants Bureau                            | 112     | 1     | 1957      |                   |
|                               |  | Doklady Earth Sciences Sections (Includes: Geochemistry, geology, geophysics, hydrogeology, mineralogy, paleontology, petrography, permafrost sections)  | American Geological Institute                 | 124     | 1     | 1959      |                   |
|                               |  | Proceedings of the Academy of Sciences of the USSR, Section: Geochemistry  | Consultants Bureau                            | 106     | 1     | 1957      |                   |
|                               |  | Proceedings of the Academy of Sciences of the USSR, Section: Geology   | Consultants Bureau                            | 106     | 1     | 1957      |                   |
|                               |  | Doklady Soviet Mathematics   | The American Mathematics Society              | 131     | 1     | 1961      |                   |
|                               |  | Soviet Physics-Doklady (Includes: Aerodynamics, astronomy, crystallography, cybernetics and control theory, electrical engineering, energetics, fluid mechanics, heat engineering, hydraulics, mathematical physics, mechanics, physics, technical physics, theory of elasticity sections) | American Institute of Physics                 | 106     | 1     | 1956      |                   |
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|                               |  |  | Consultants Bureau                            | 1       |       | 1952      |                   |
| Derevoobrabat. prom-st'       | Derevoobrabat'yayushchaya promyshlennost'        |  |   |         |       |           |                   |
| Élektrosvyaz                  | Élektrosvyaz                                     |  |   |         |       |           |                   |
| Éntom(ol). oboz(renie)        | Entomologicheskoe obozrenie                      |  |   |         |       |           |                   |
| Farmakol. (i) toksikol(ogiya) | Farmakologiya i toksikologiya                    |  |   |         |       |           |                   |
| FMM                           | Fizika metallov i metallovedenie                 |  |   |         |       |           |                   |
| Fiziol. zhurn. SSSR           | Fiziolicheskie zhurnali im. I. M. Sechenova      |  |   |         |       |           |                   |
| (im. Sechenova)               | Fiziologiya rastenii                             |  |   |         |       |           |                   |
| Fiziol(ogiya) rast.           | Geokhimiya                                       |  |   |         |       |           |                   |
| FTT                           | Fizika tverdogo tela                             |  |   |         |       |           |                   |
| Izmerit. tekhnika             | Izmeritel'naya tekhnika                          |  |   |         |       |           |                   |
| Izv. AN SSSR,                 | Izvestiya Akademii Nauk SSSR:                    |  |   |         |       |           |                   |
| O(td). Kh(im). N(auk)         | Otdelenie khimicheskikh nauk                     |  |   |         |       |           |                   |

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|--|---|--|----|------|
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|  | Metallurgiya i topliva  | Russian Metallurgy and Fuels   | 1  | 1960 |
|  | Mikrobiologiya  | Microbiology   | 26 | 1957 |
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|  | Prirodoostroenie  | Instrument Construction  | 1  | 1958 |
|  | Pribory i tekhnika eksperimenta   | Instruments and Experimental Techniques                                    | 1  | 1959 |
|  | Prikladnaya matematika i mekhanika  | Applied Mathematics and Mechanics  | 1  | 1957 |
|  | (see Pribory i tekhn. éks.)   |  |    |      |
|  | Problemy Severa   | Problems of the North  |    |      |
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